Permit Application

Environmental Impact Assessment

White Pine North Project

Volume IIF

Appendix C-1 (6 of 6)

White Pine Copper LLC

White Pine, Michigan

September 2026

Project I.D.: 23W200

Solving our clients' toughest science and engineering challenges.

C-1

Groundwater and Surface Water Hydrology Baseline Report

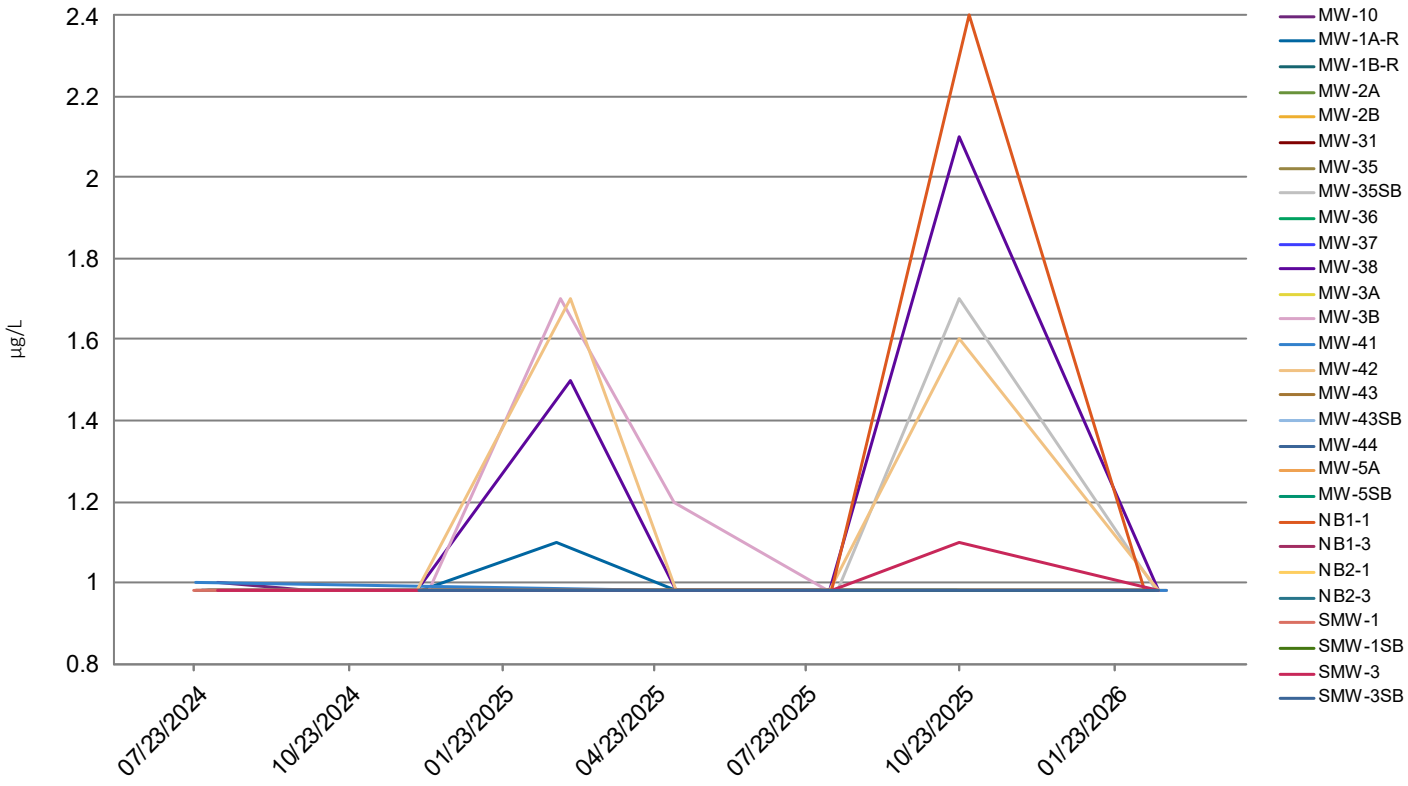
(6 of 6)

Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

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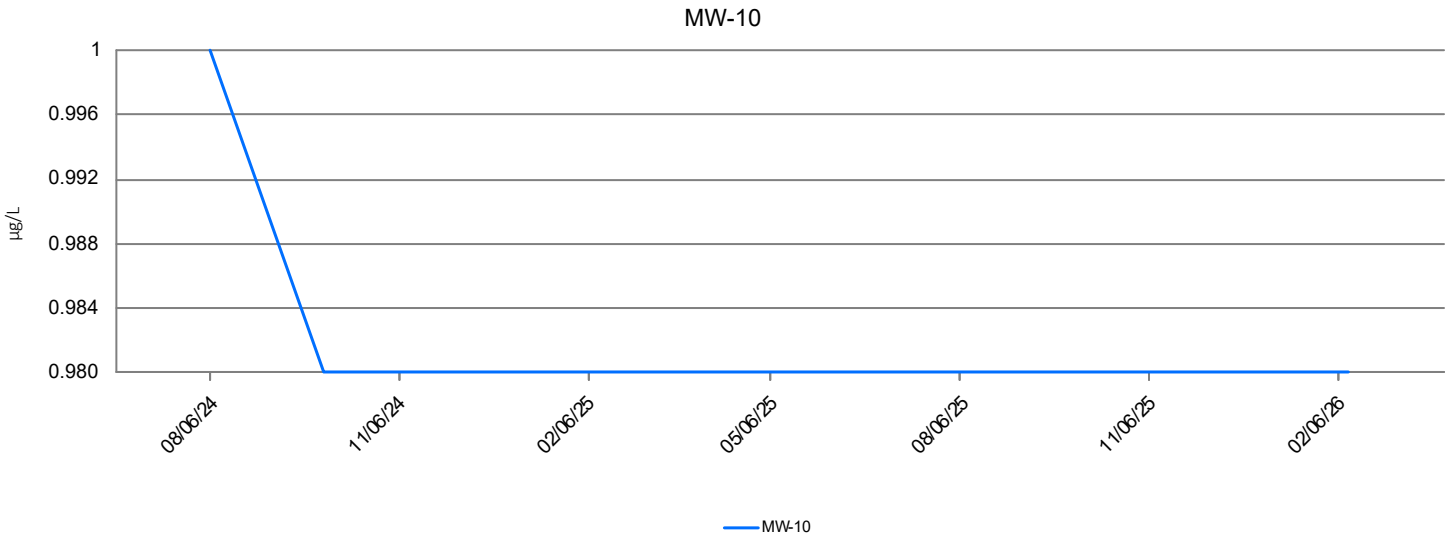


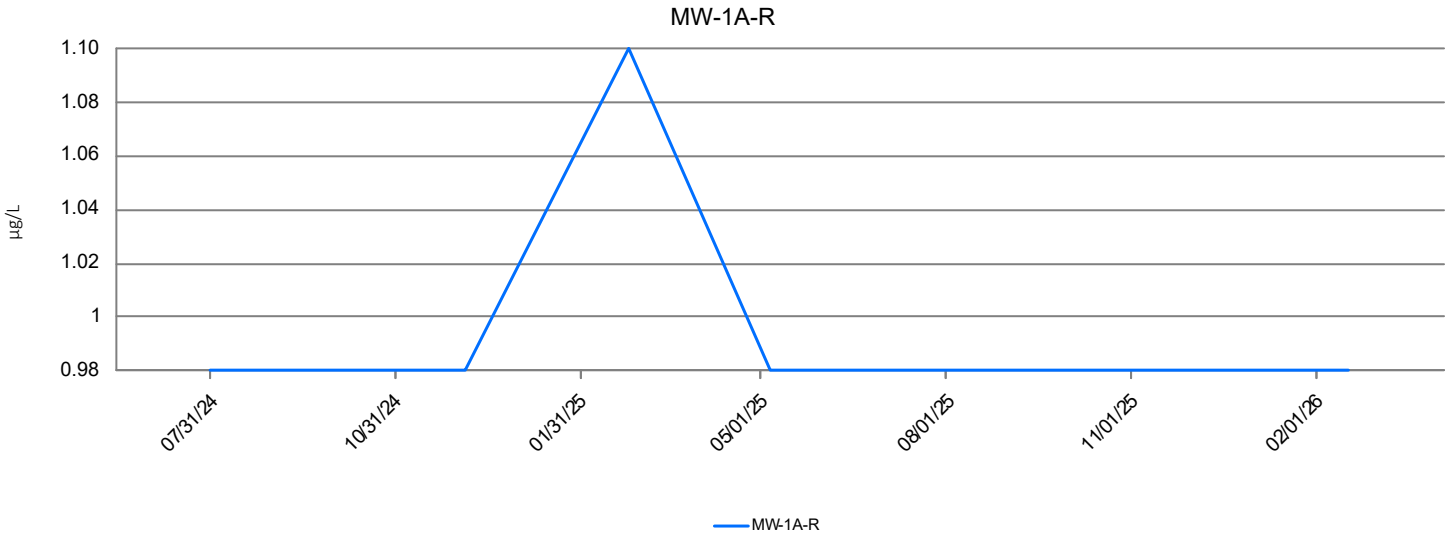
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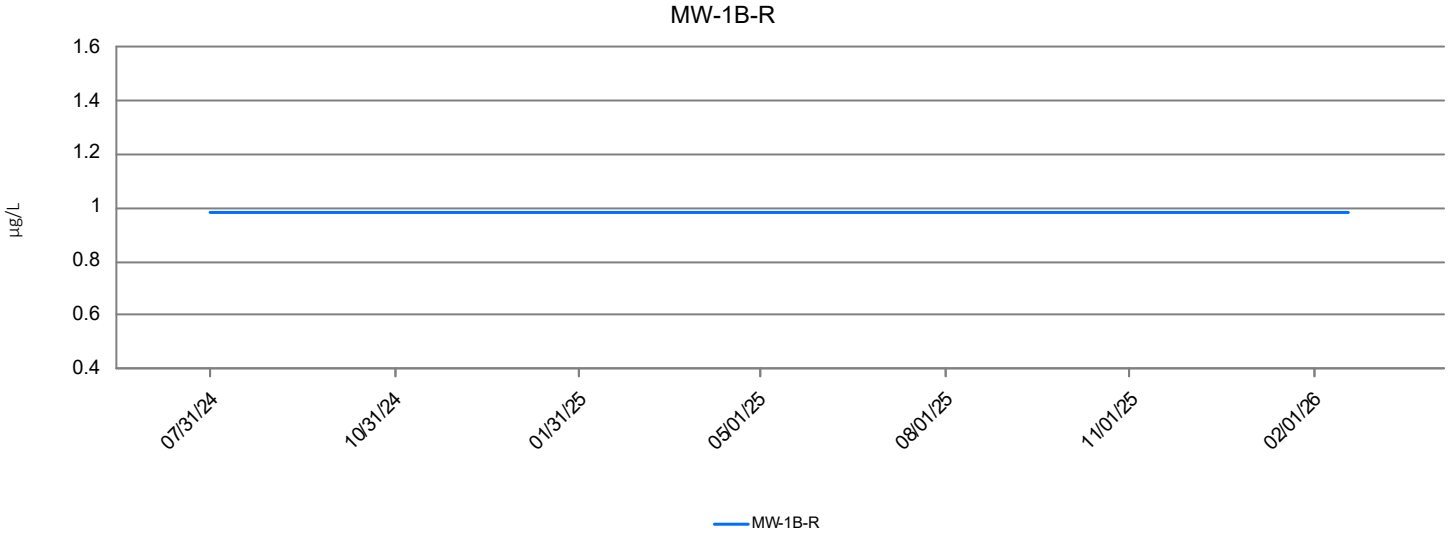
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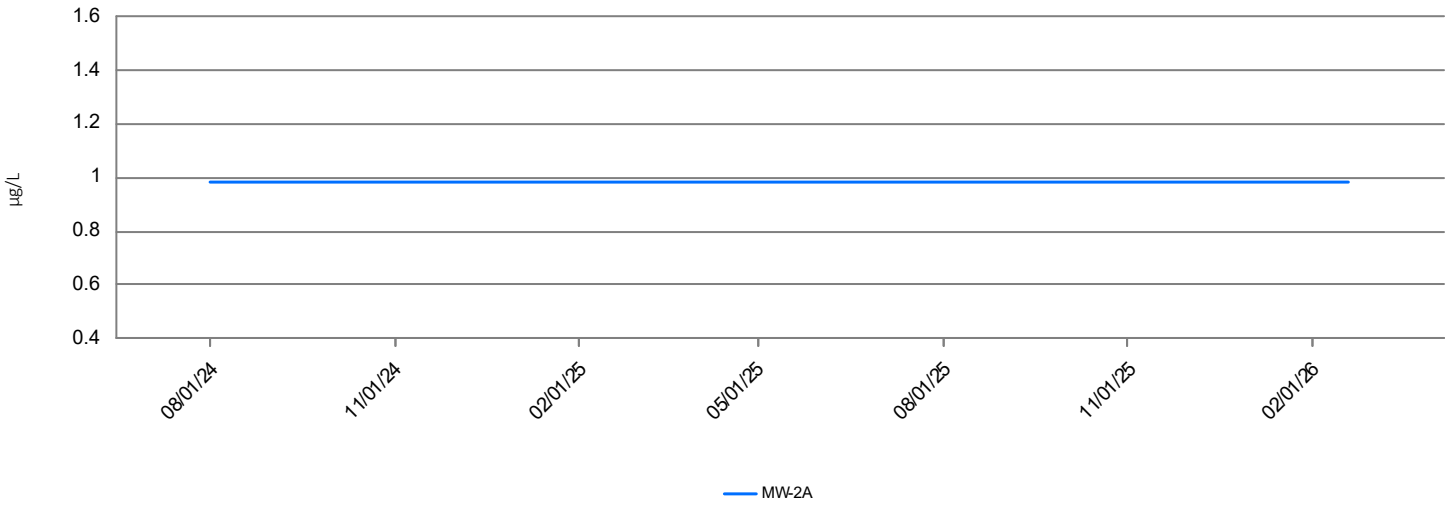
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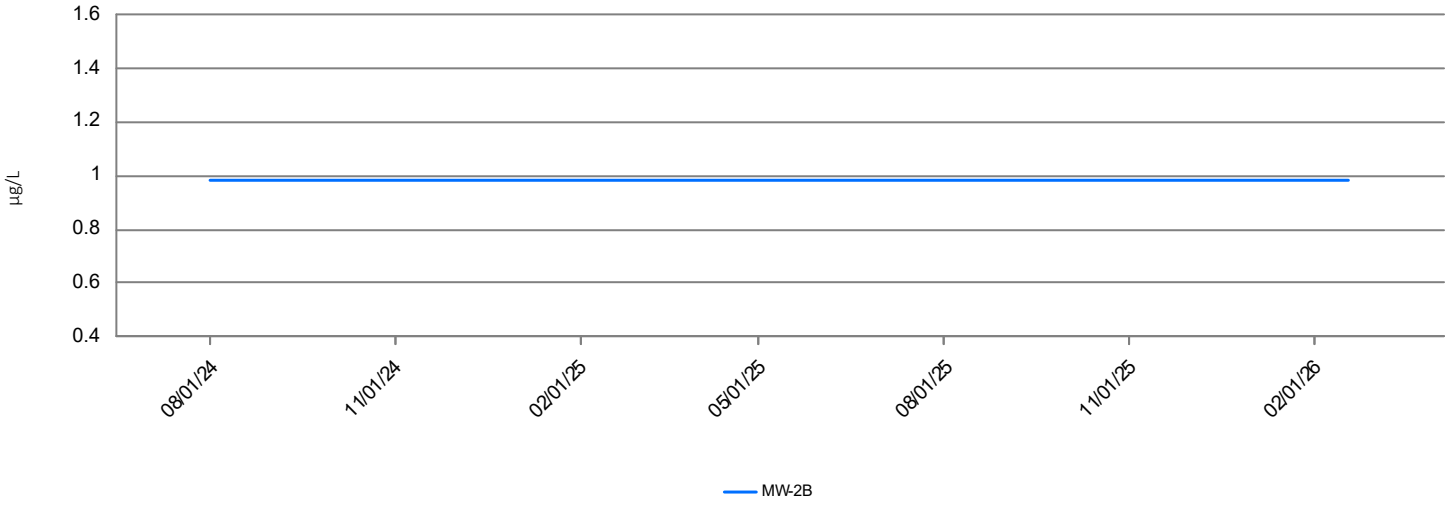
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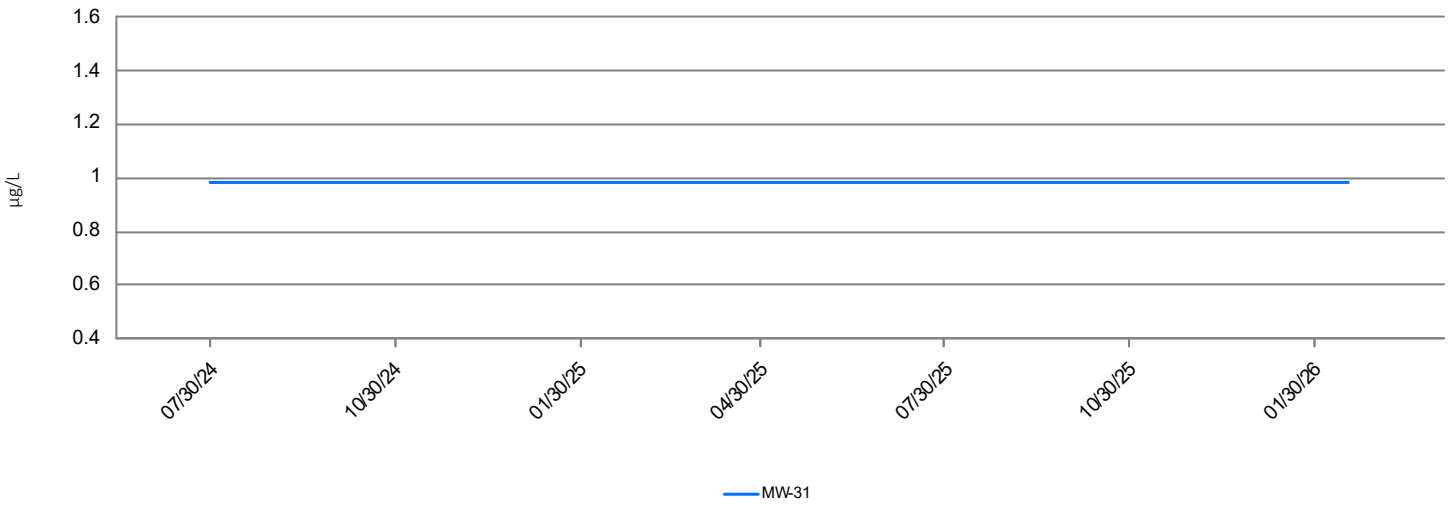
MW-2A



MW-2B



MW-31

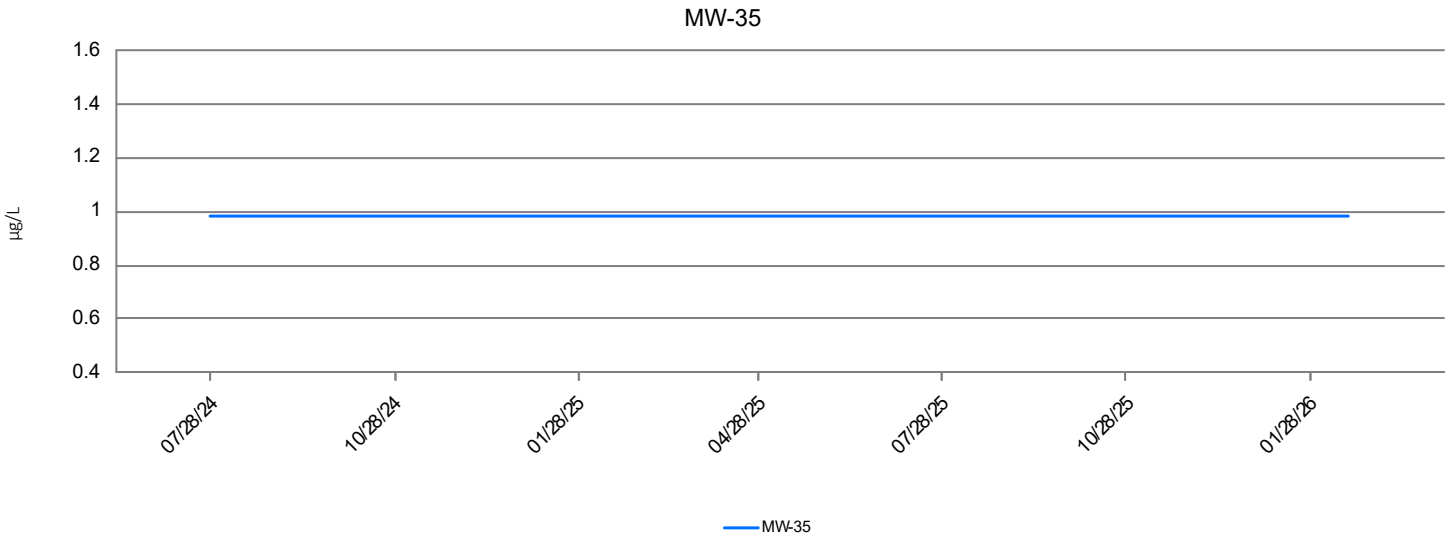


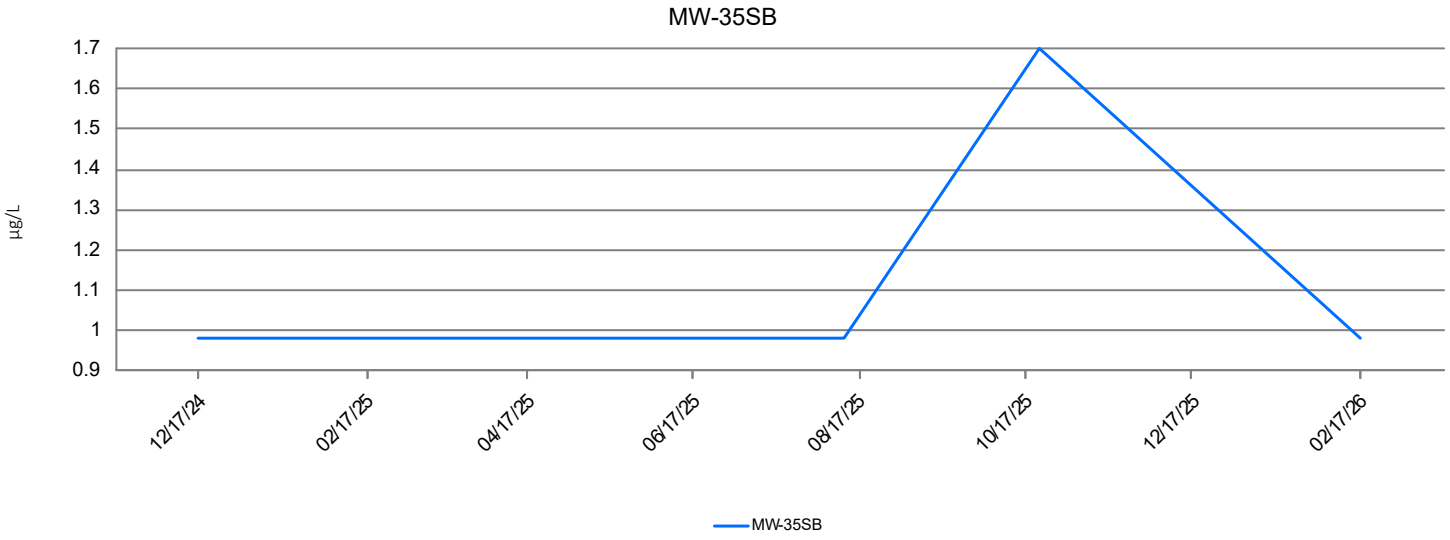
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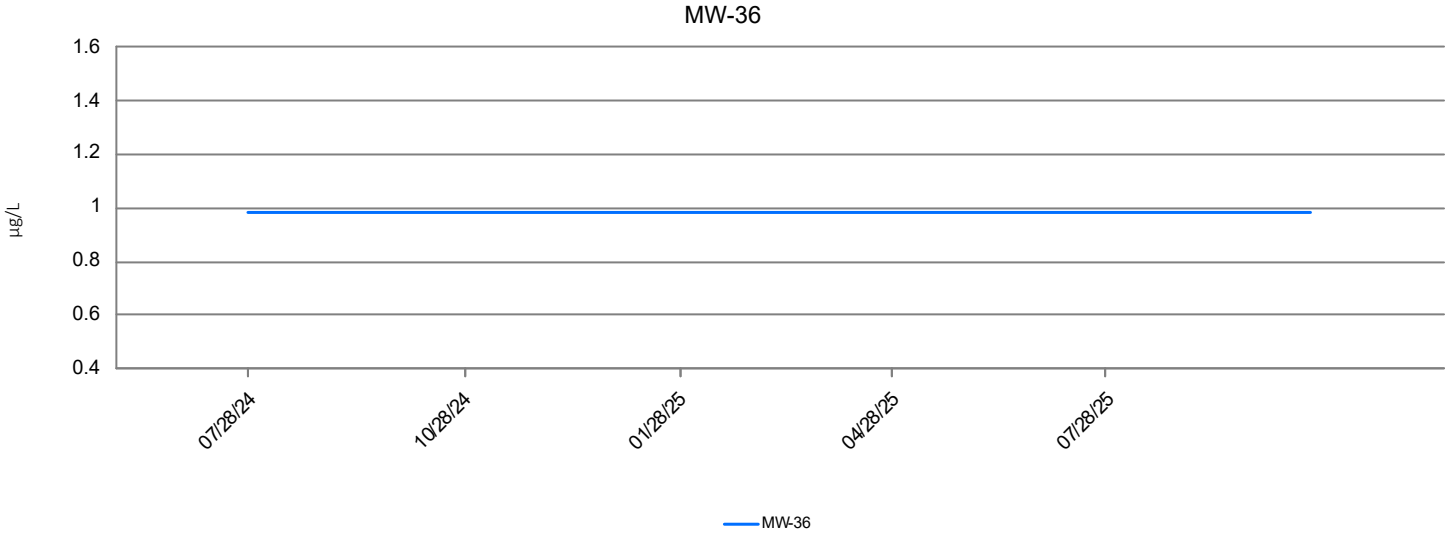
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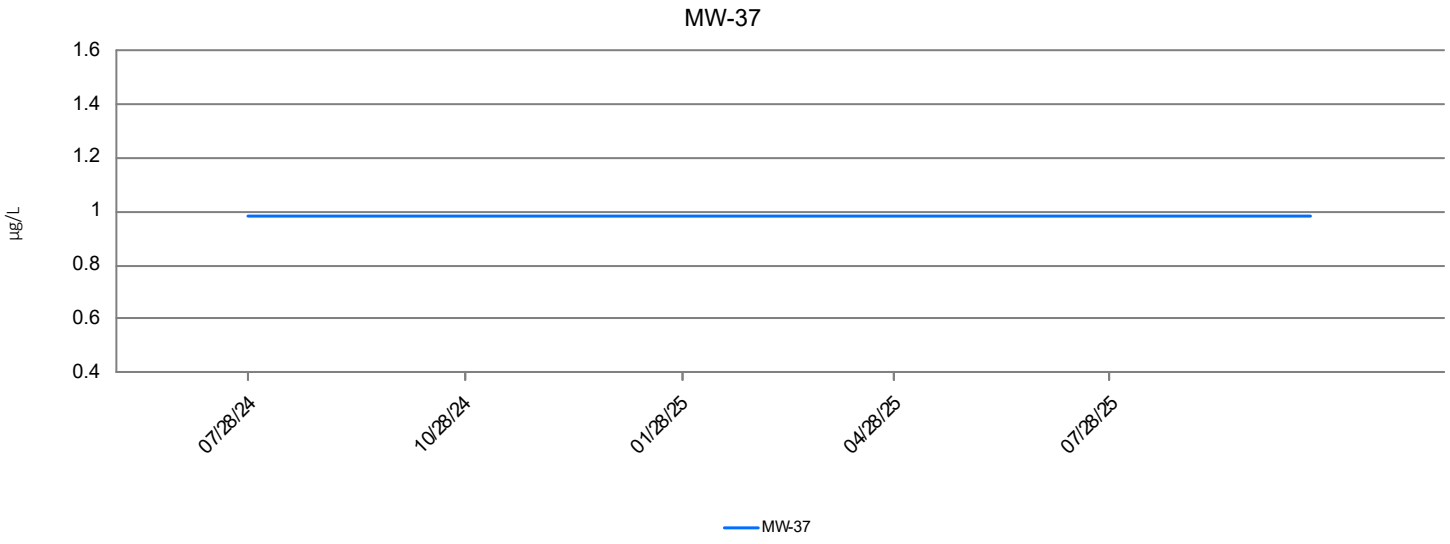


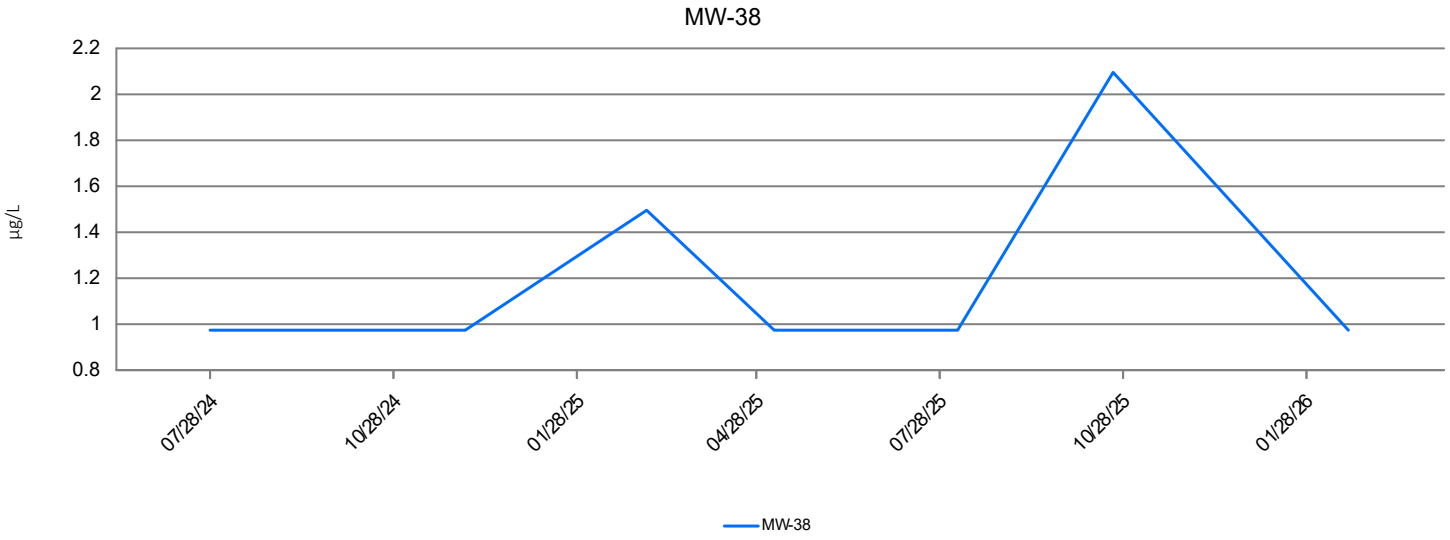
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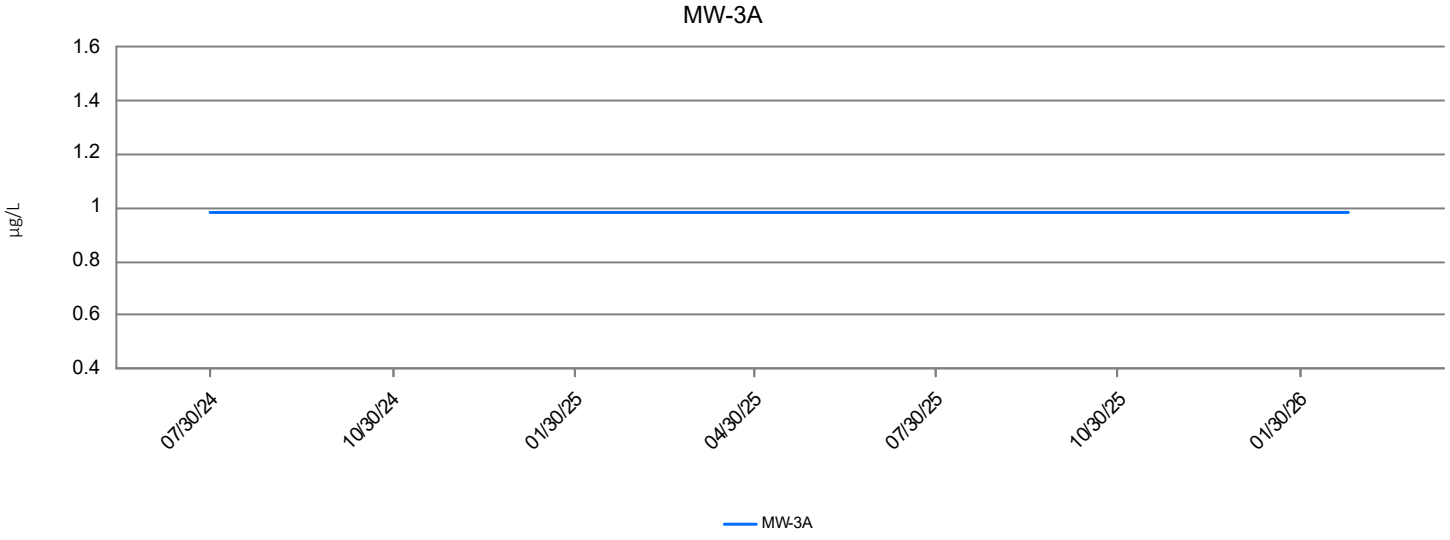
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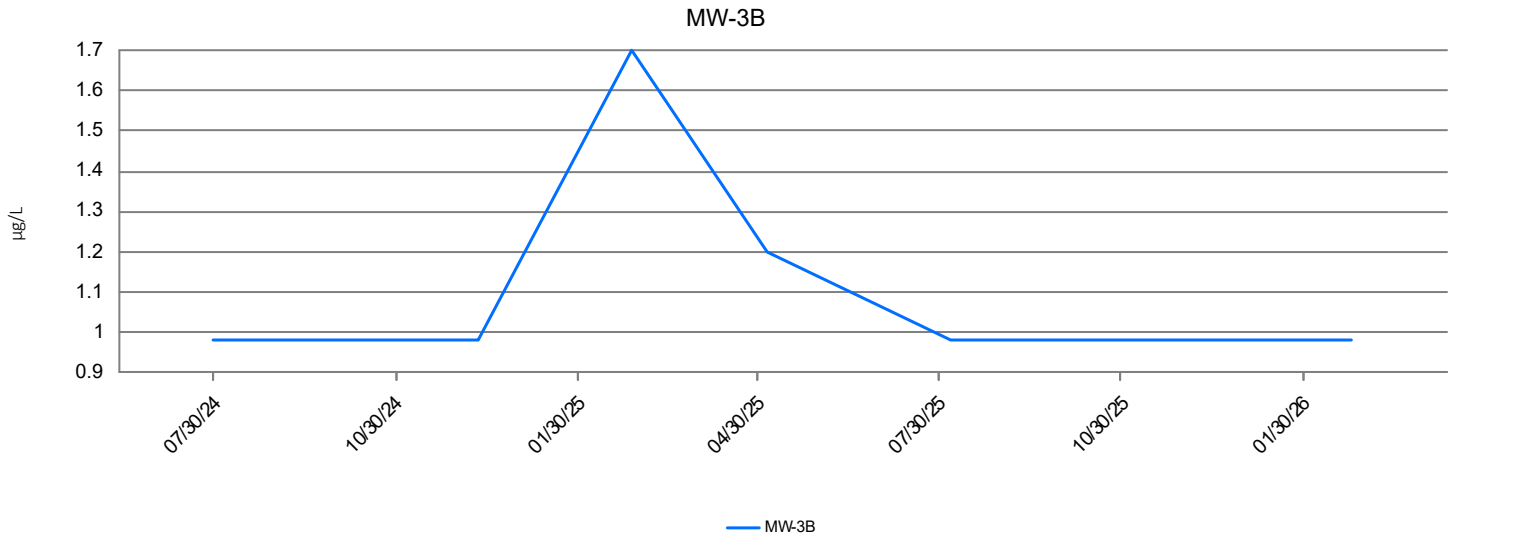


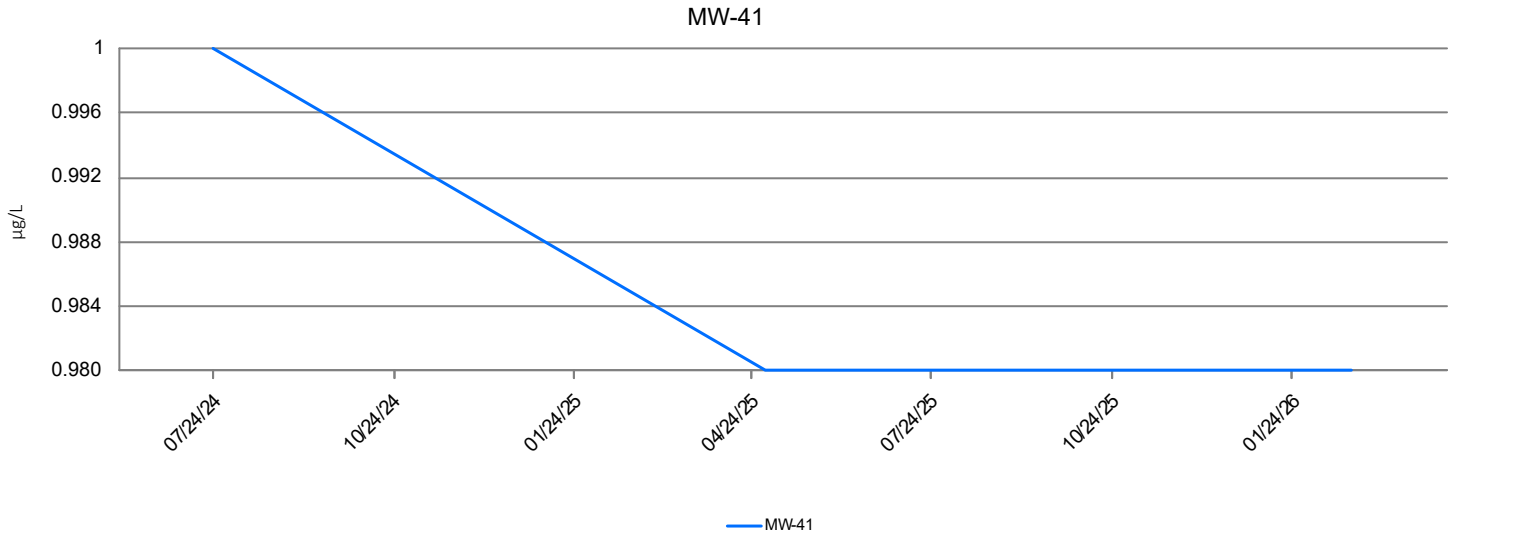
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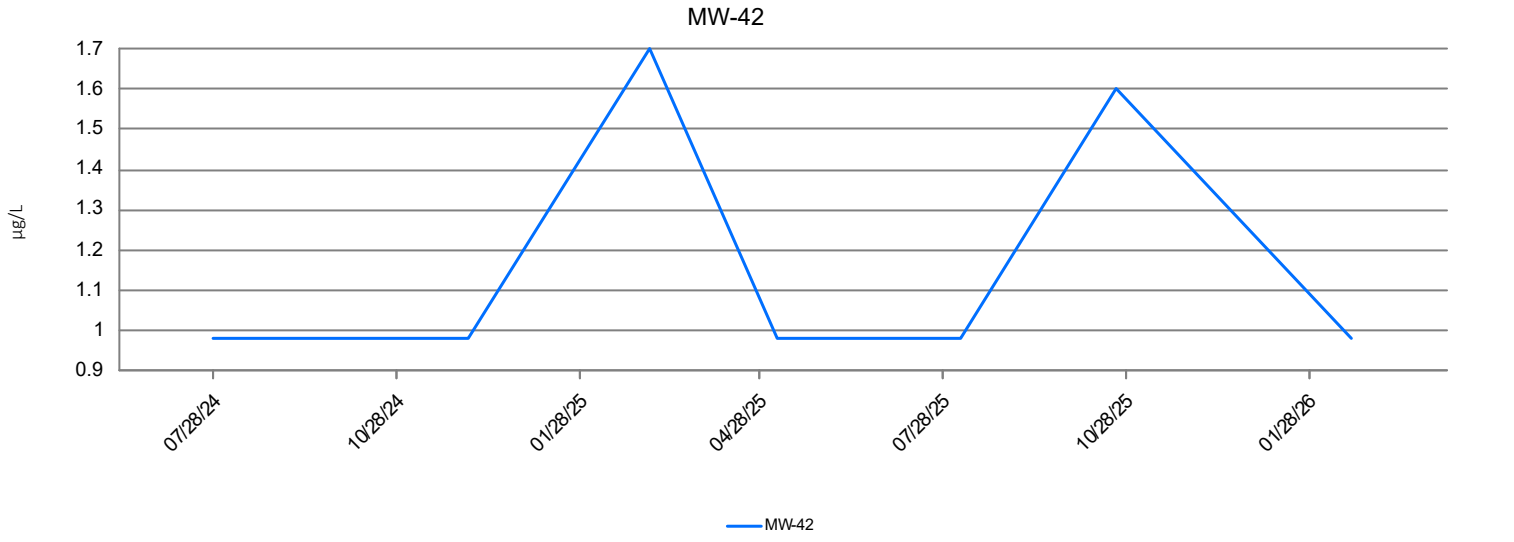
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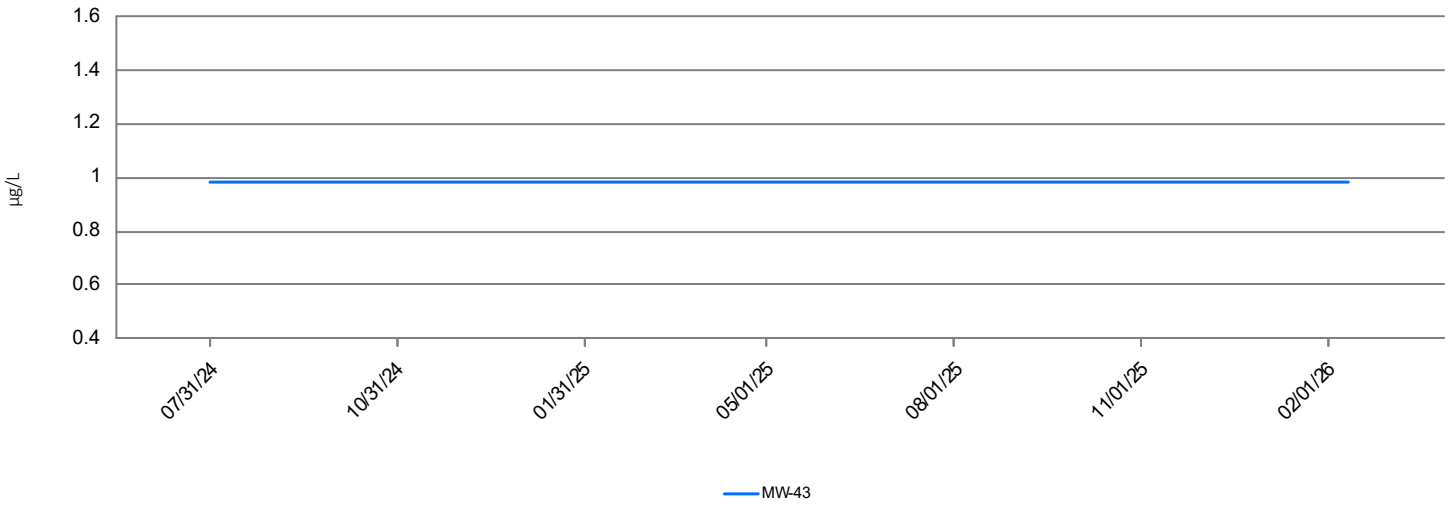
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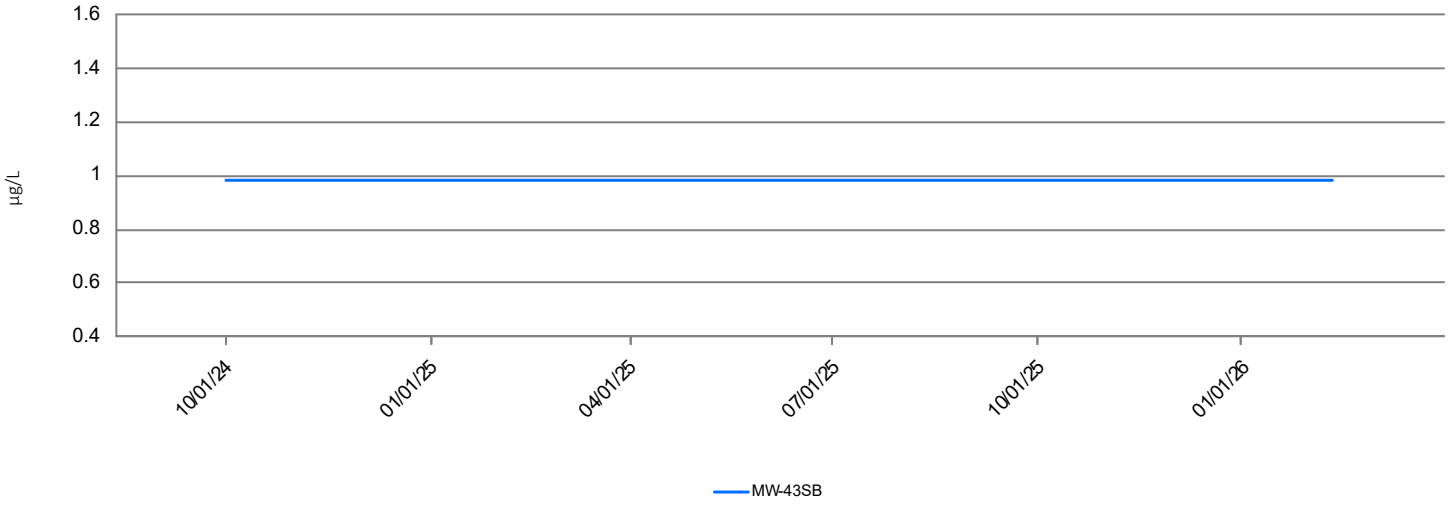
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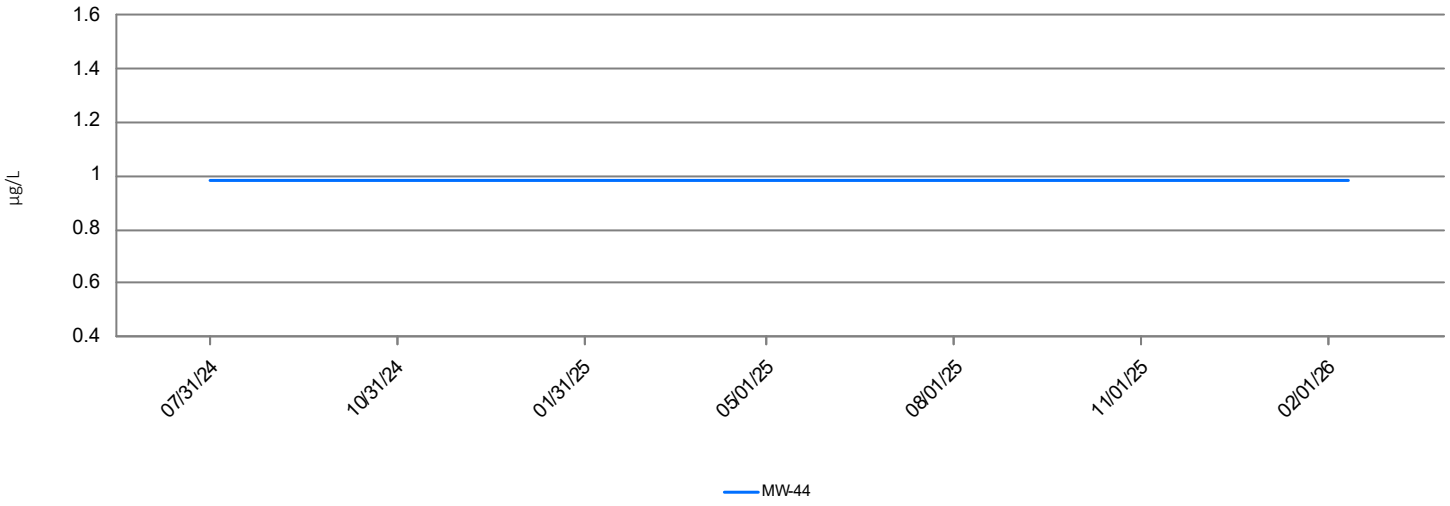
MW-43



MW-43SB



MW-44



Printed Date: 05/21/2026

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MCERTS Cert. no. Sira MC090140/02

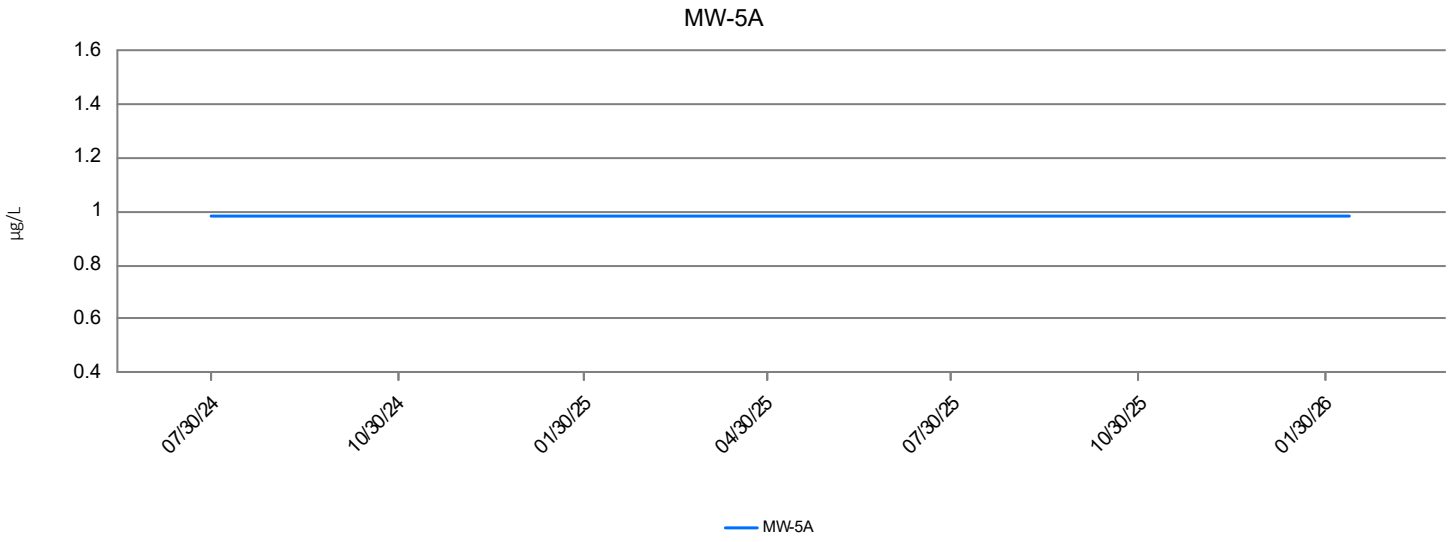
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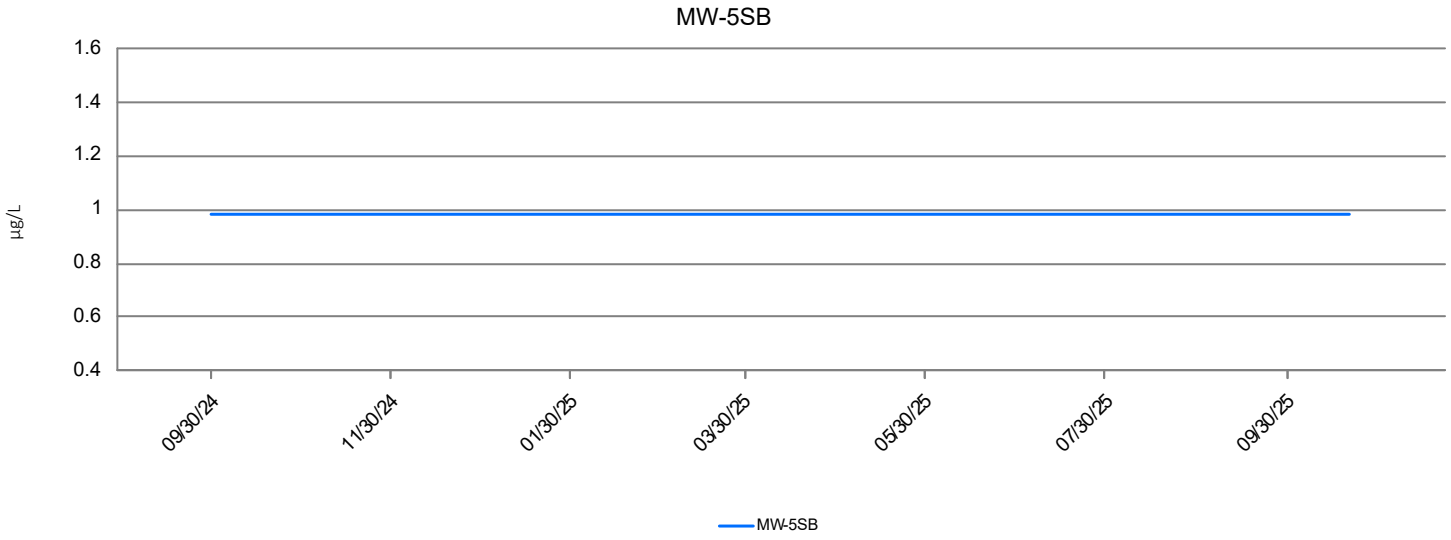
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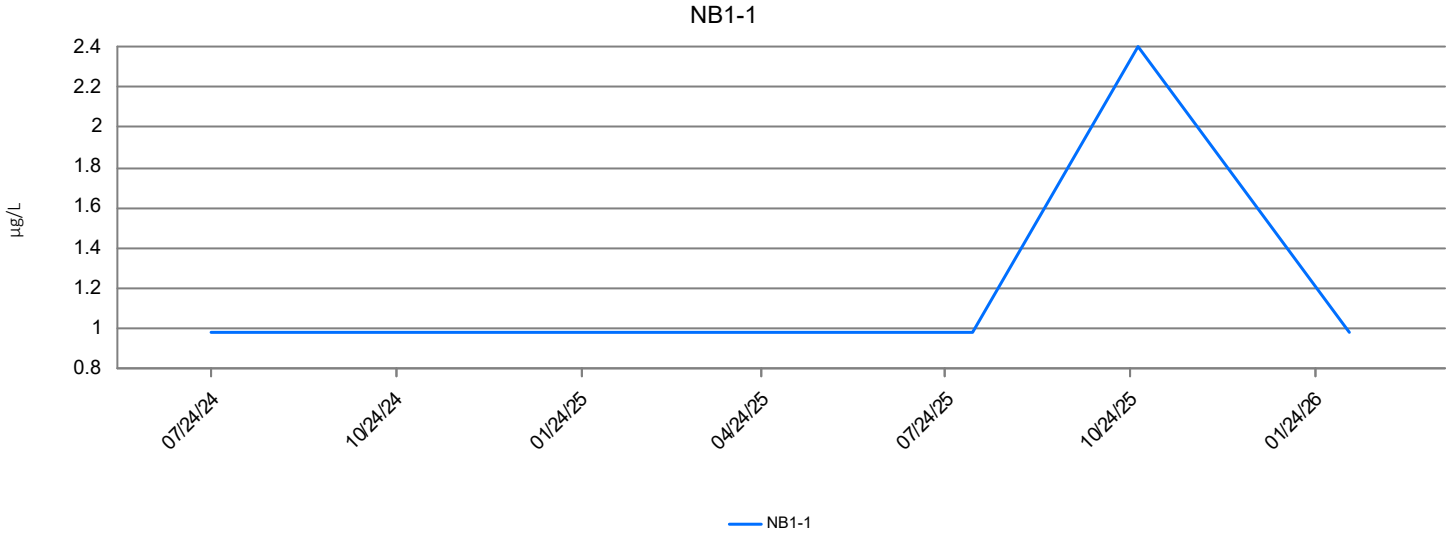
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MonitorPro

No Group Selected, Selenium, Dissolved (µg/L)







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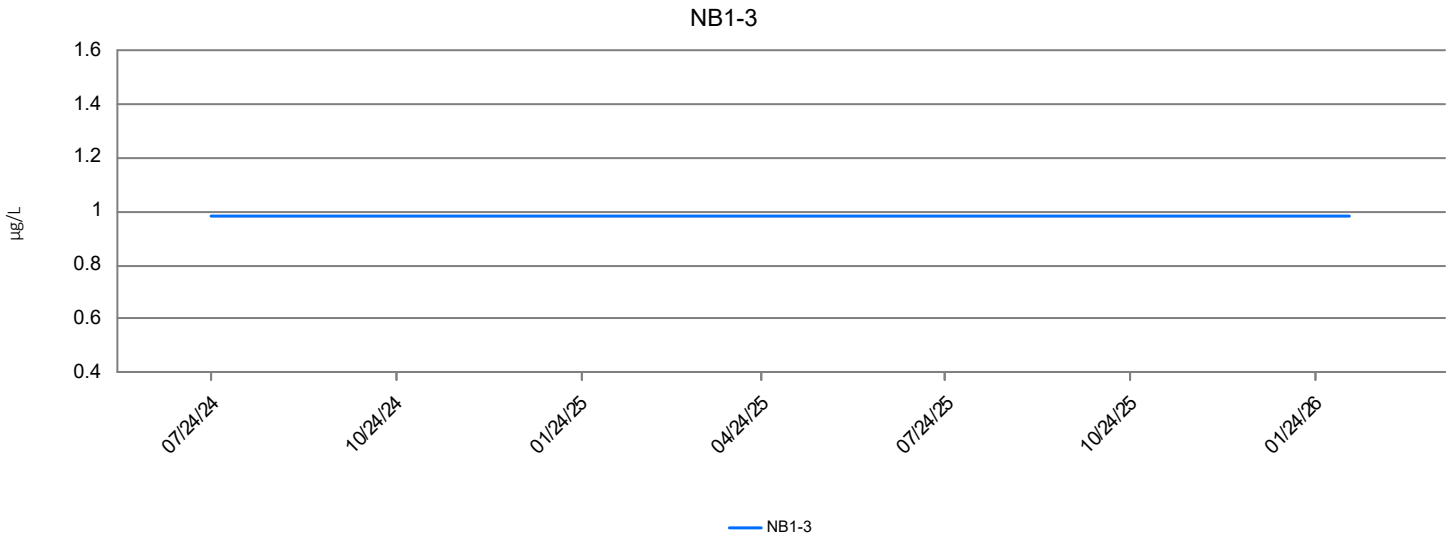
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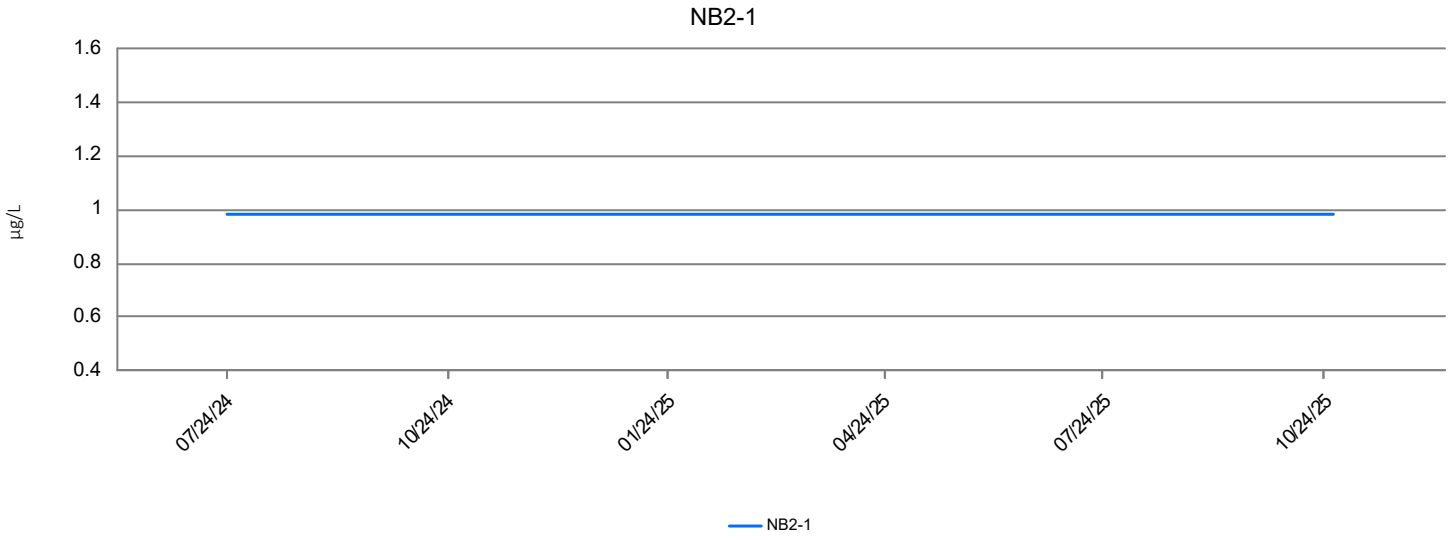
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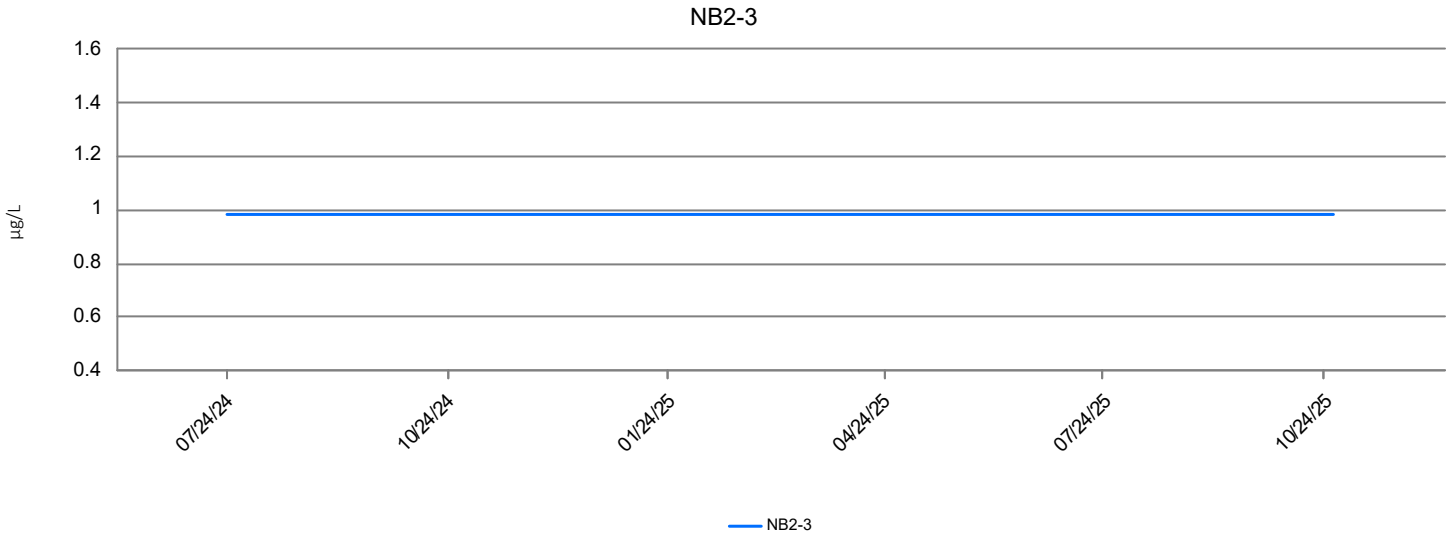
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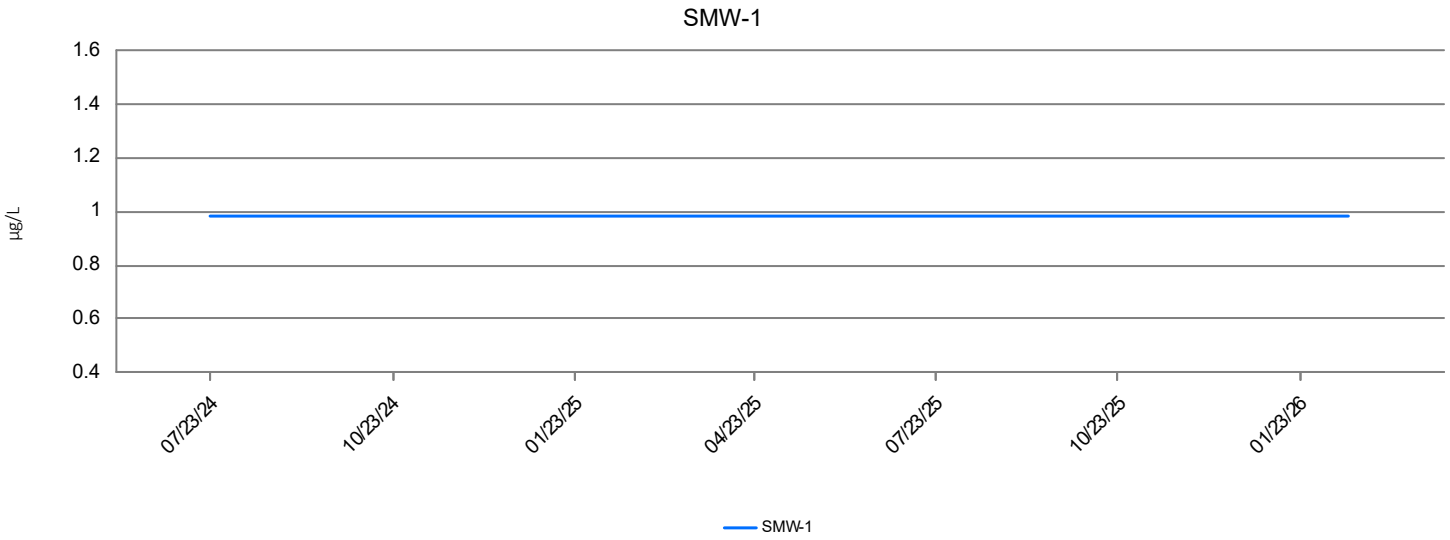


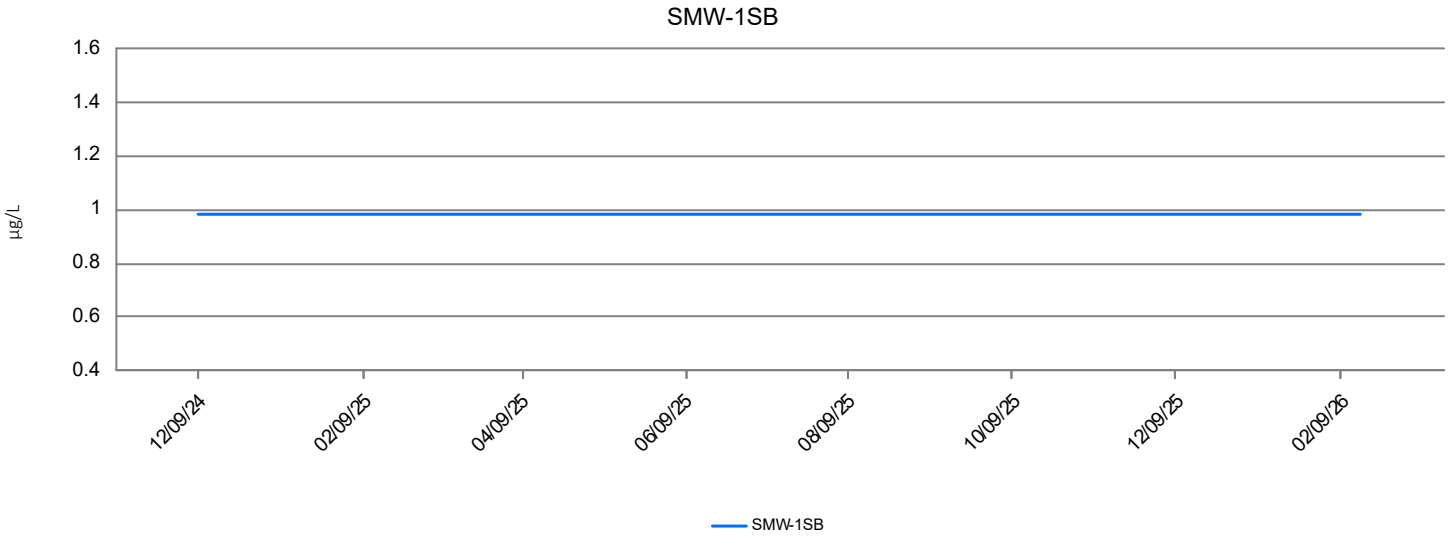
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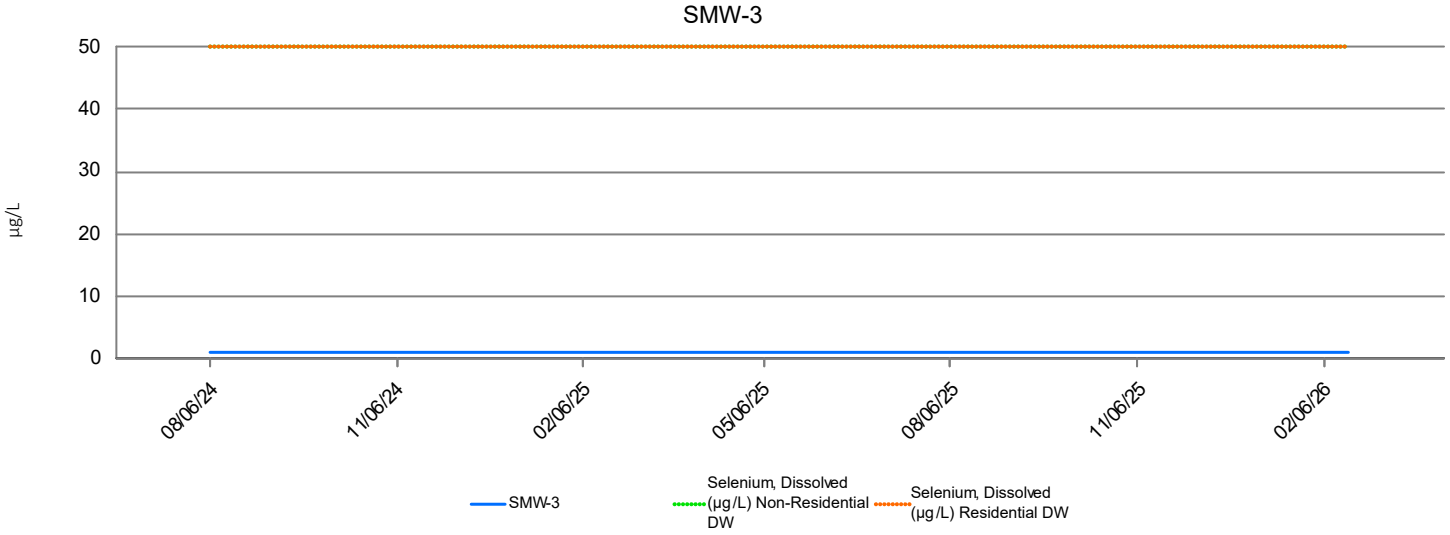
Date from 07/01/2024 to 05/01/2026

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No Group Selected, Selenium, Dissolved (µg/L)







Printed Date: 05/21/2026

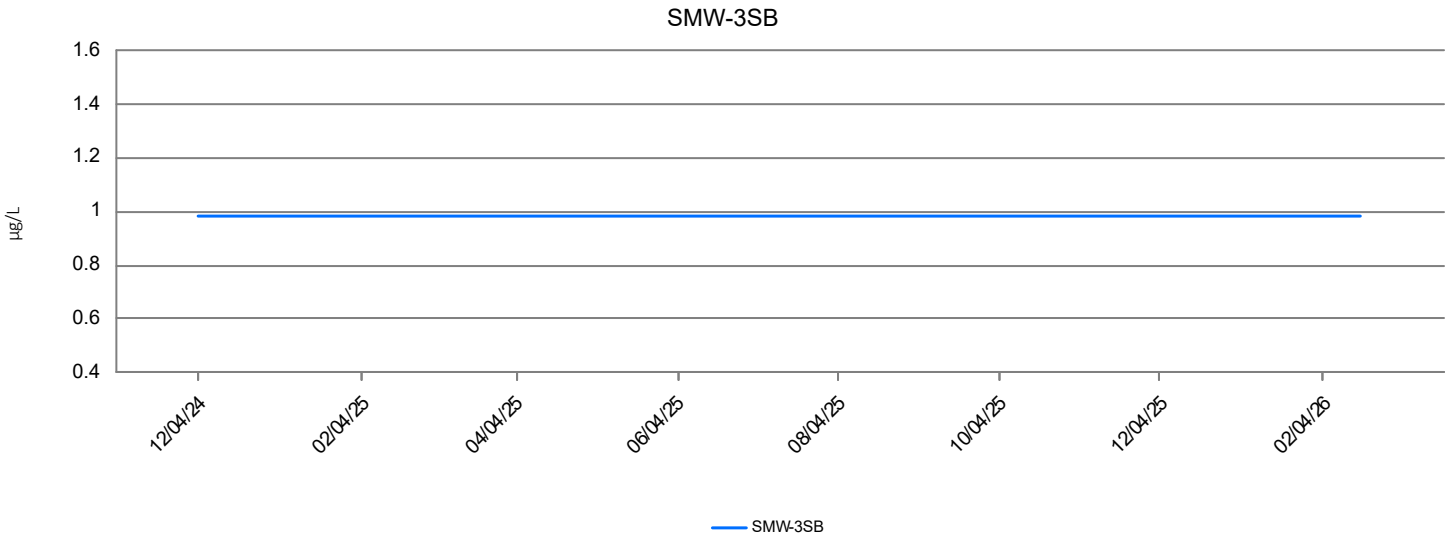
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Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

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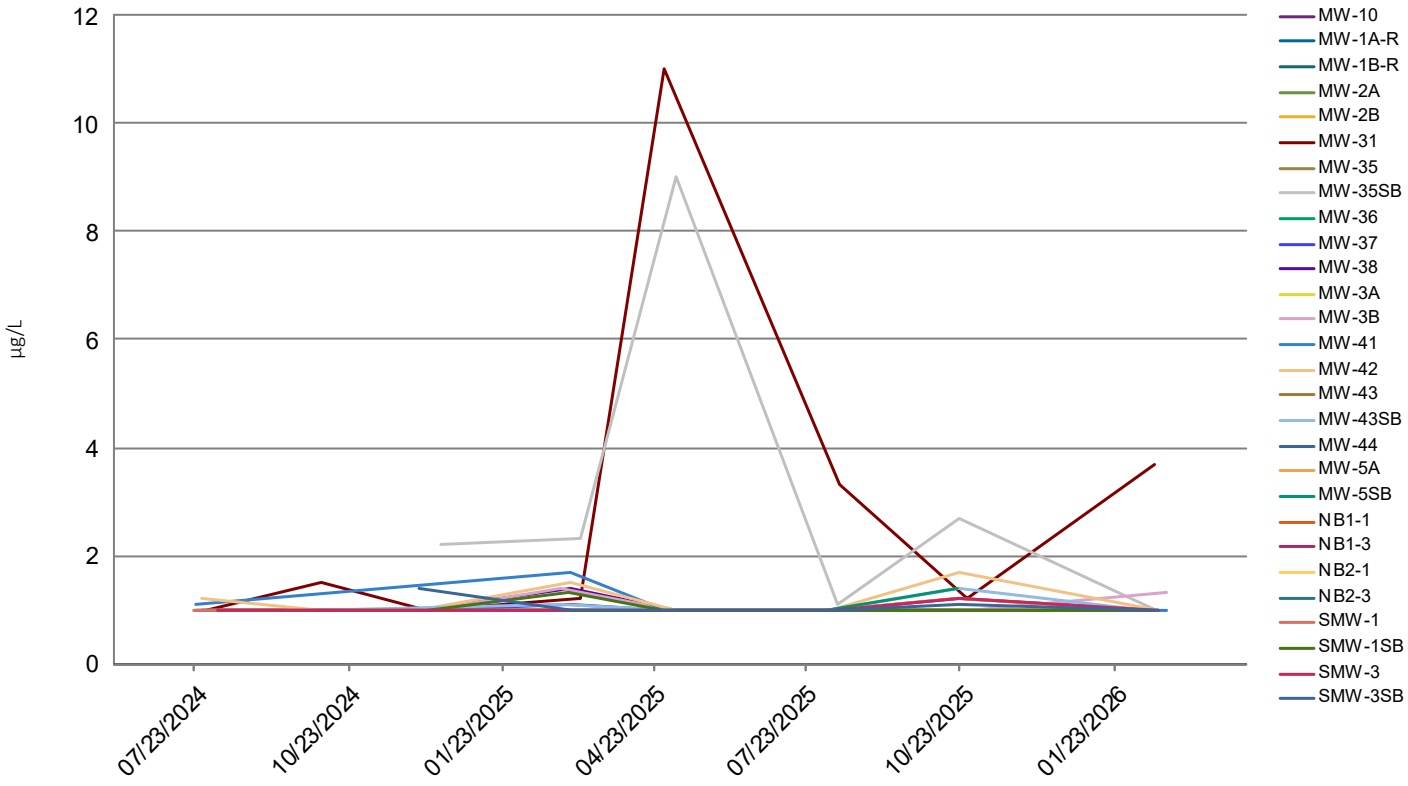


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

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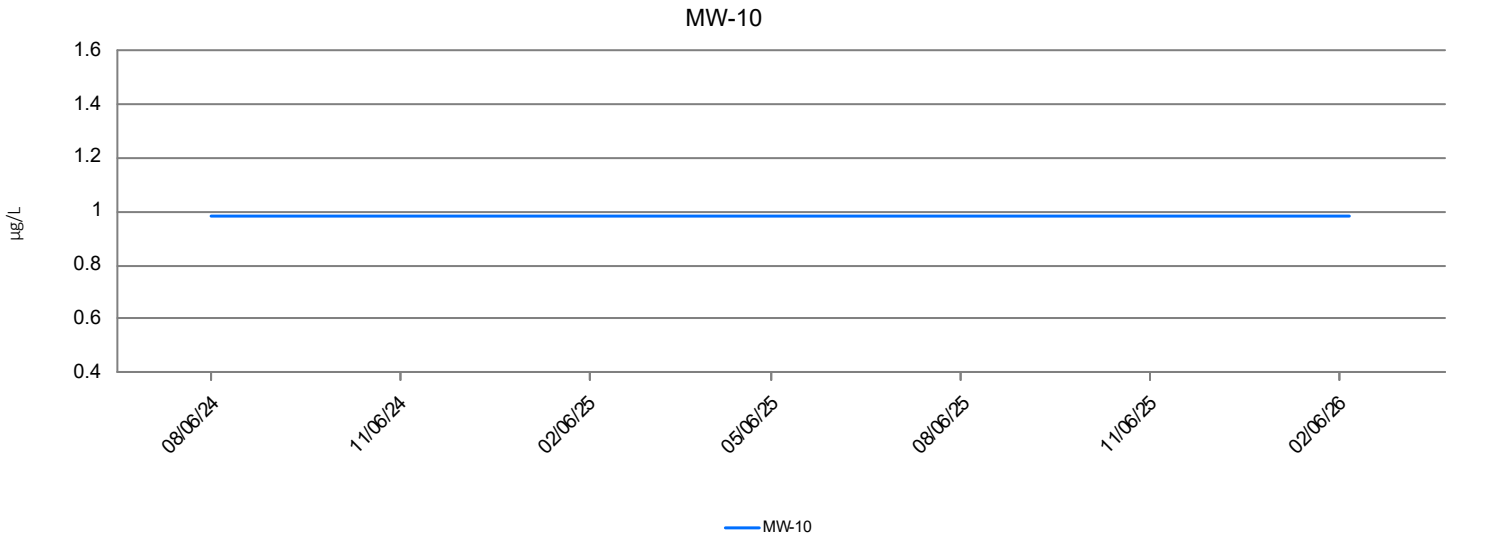


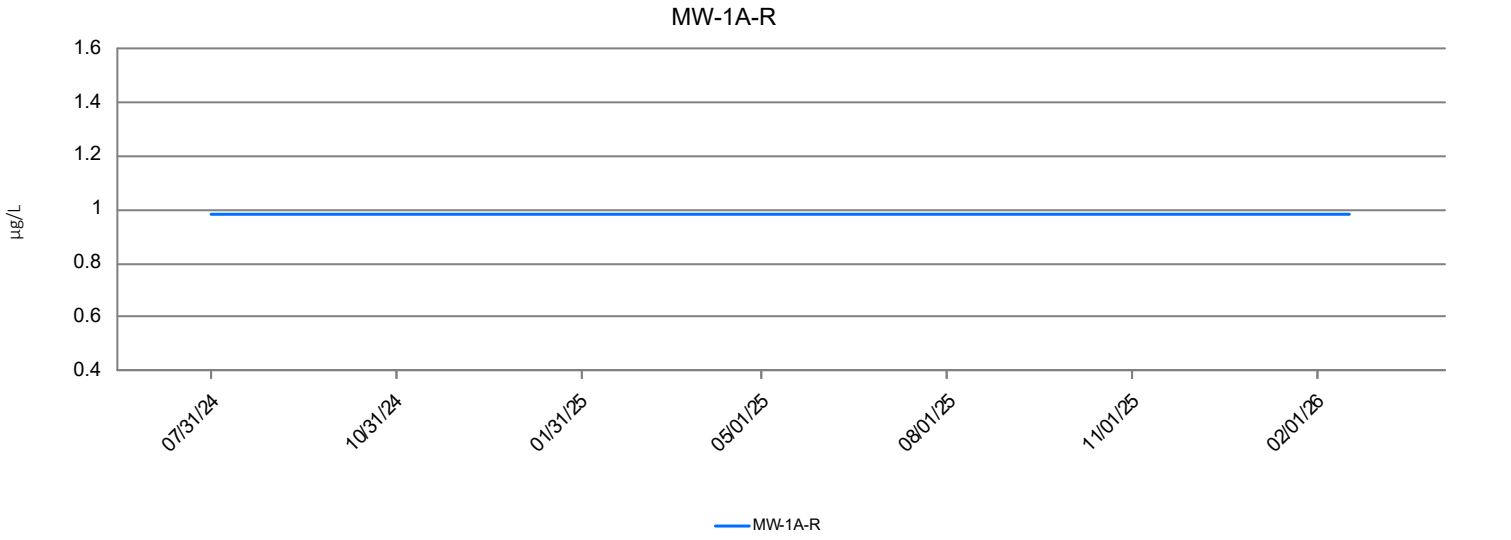
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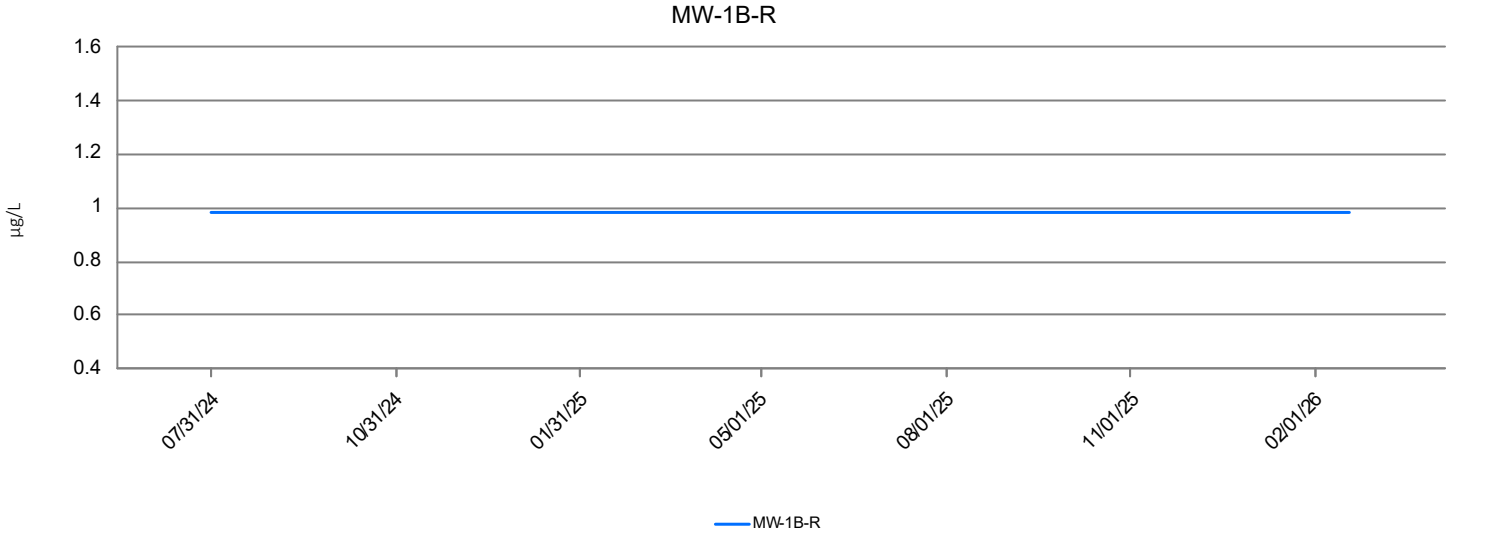
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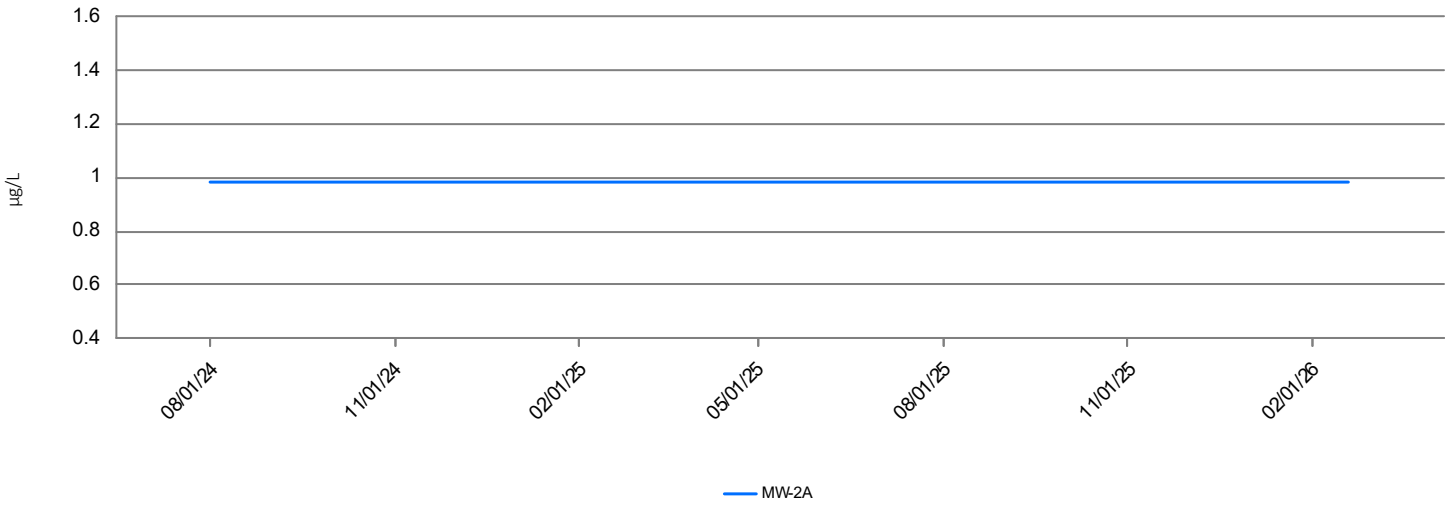
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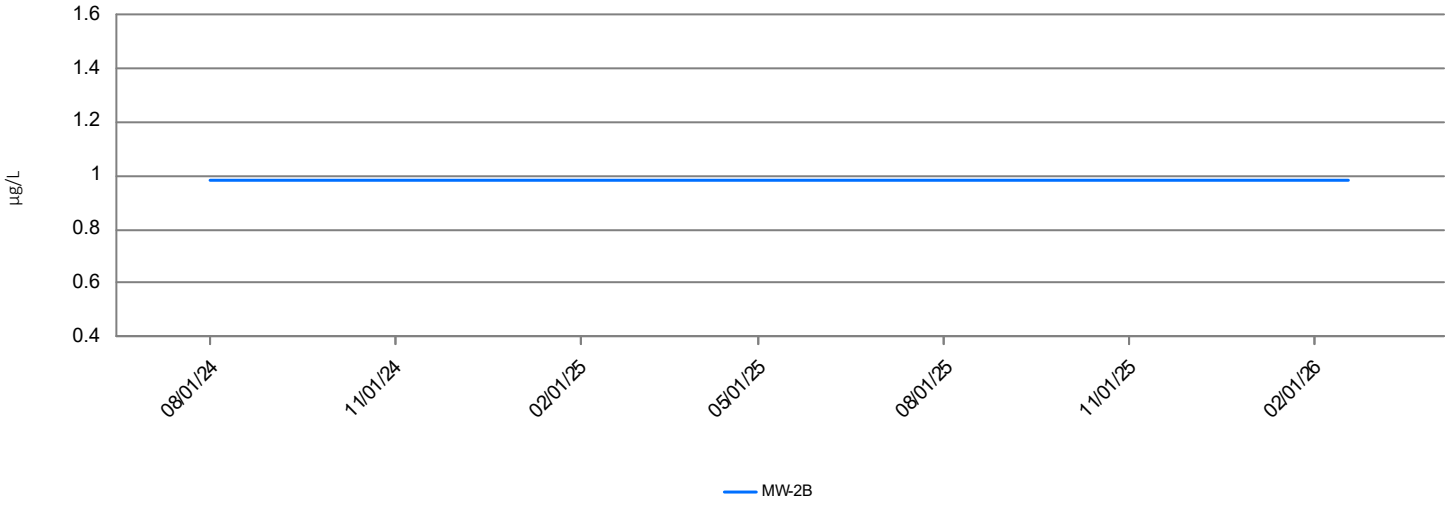
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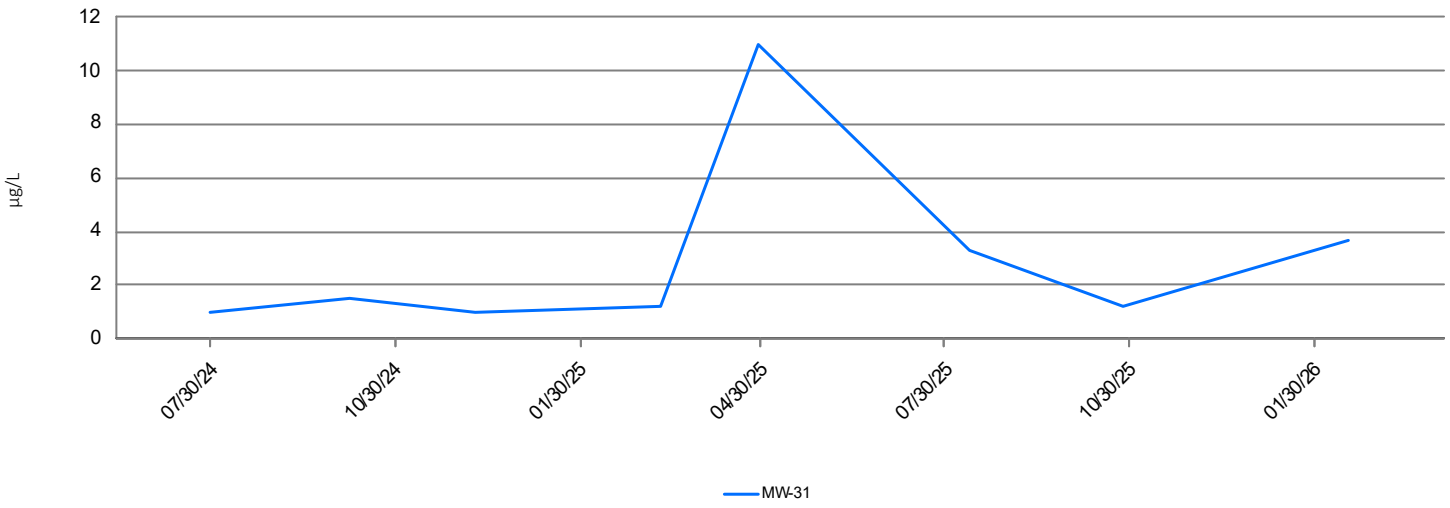
MW-2A



MW-2B



MW-31

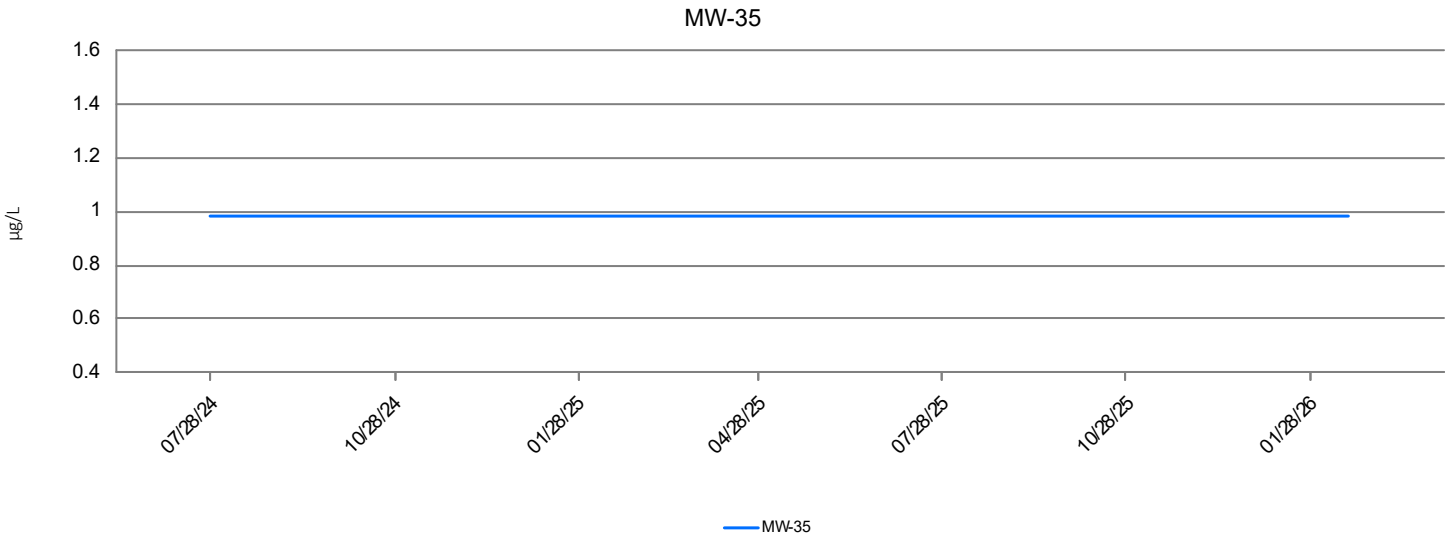


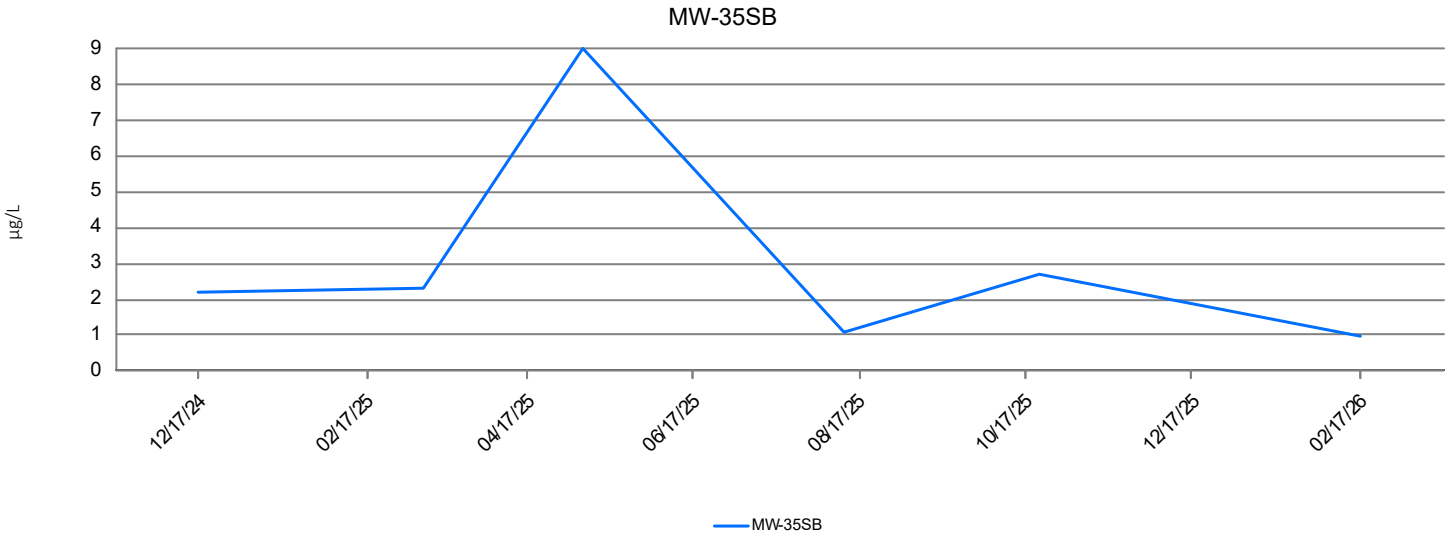
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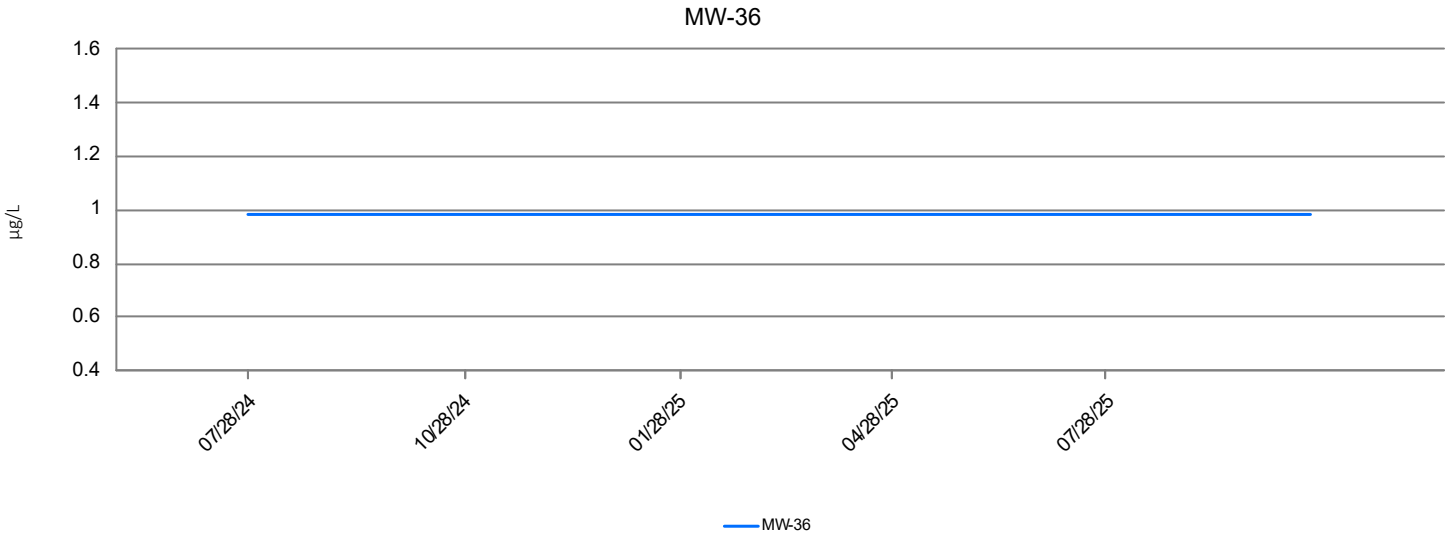
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Selenium, Total Recoverable (µg/L)







Printed Date: 05/21/2026

EHS DATA

MCERTS Cert. no. Sira MC090140/02

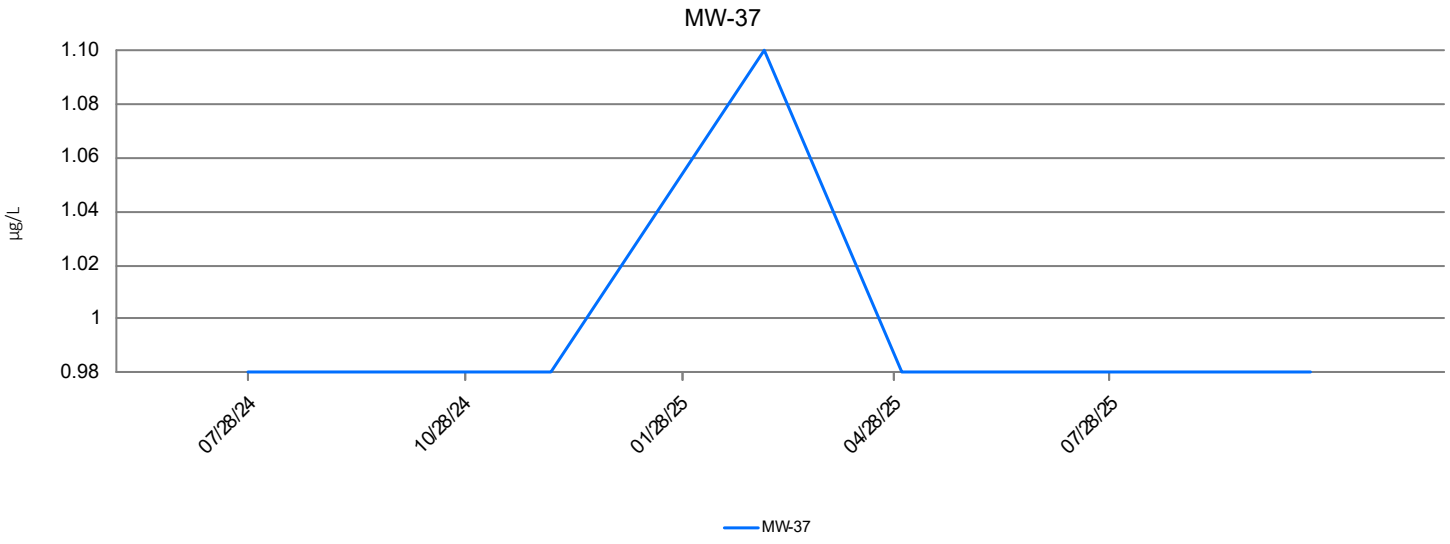
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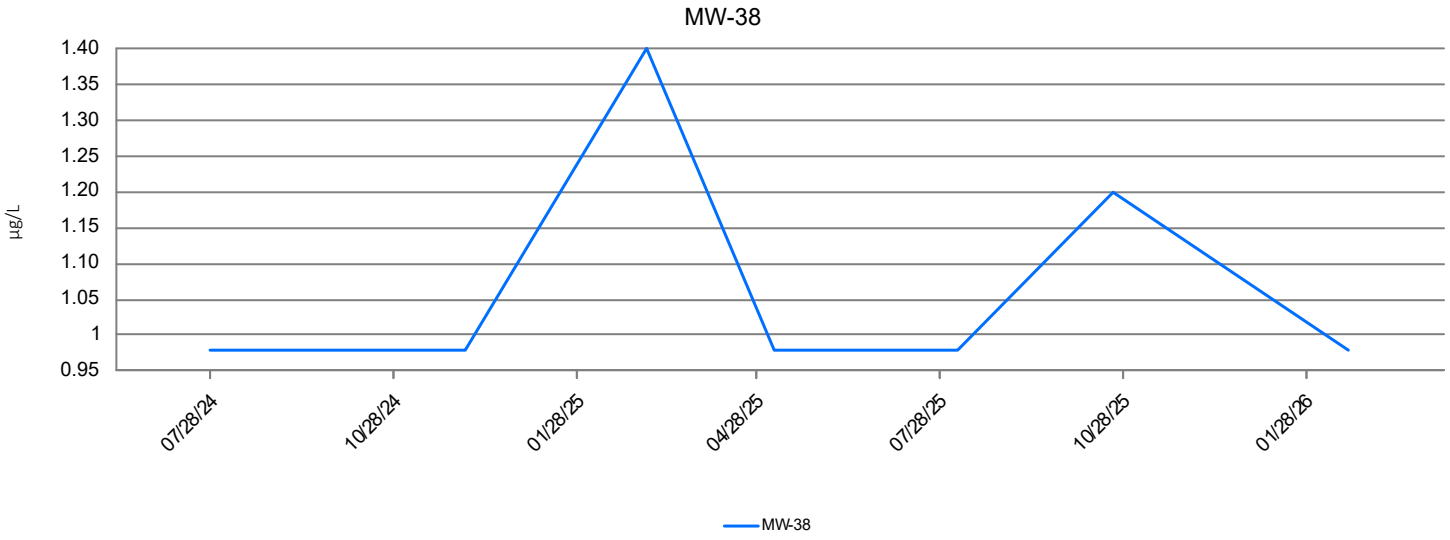
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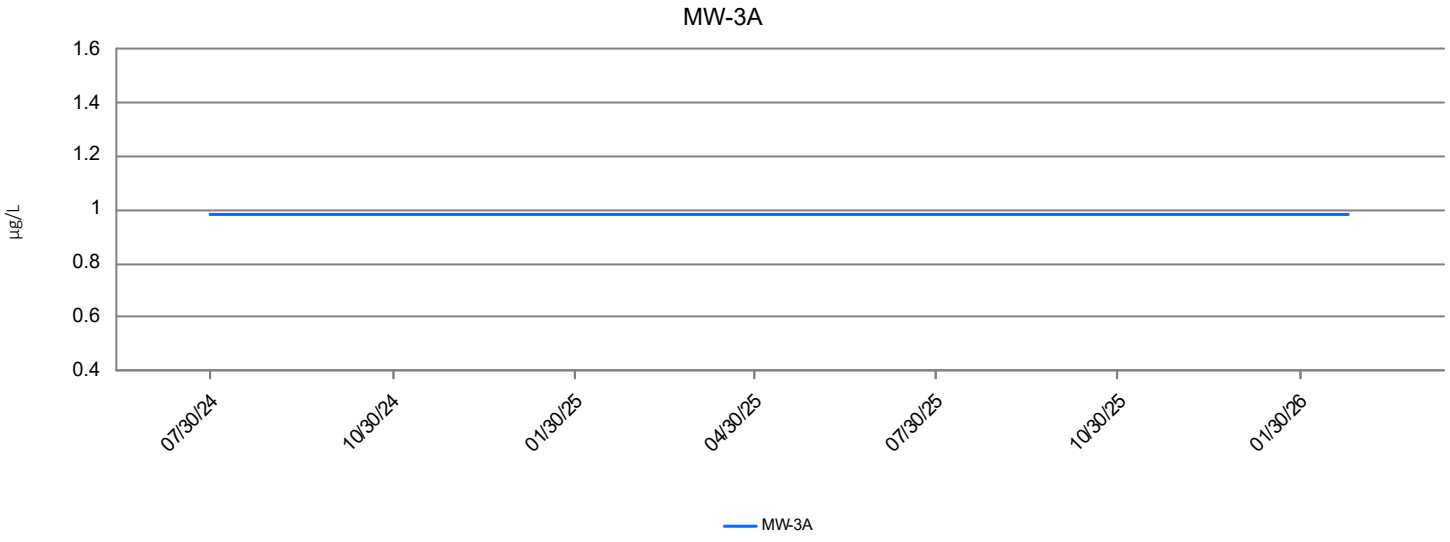
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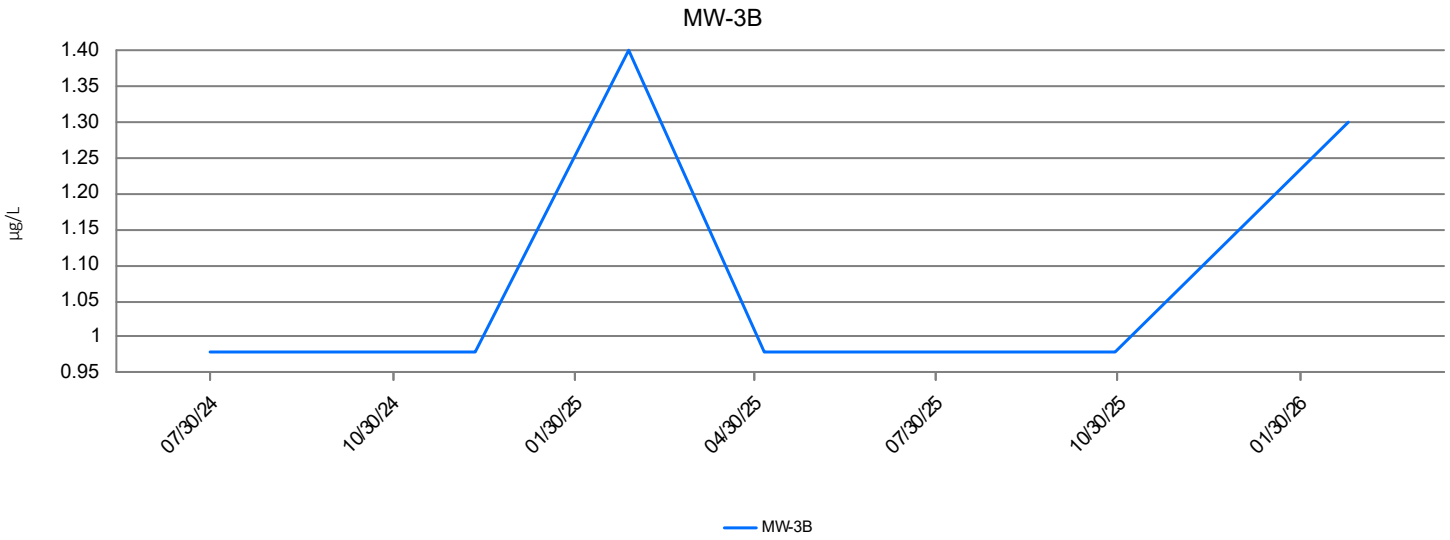


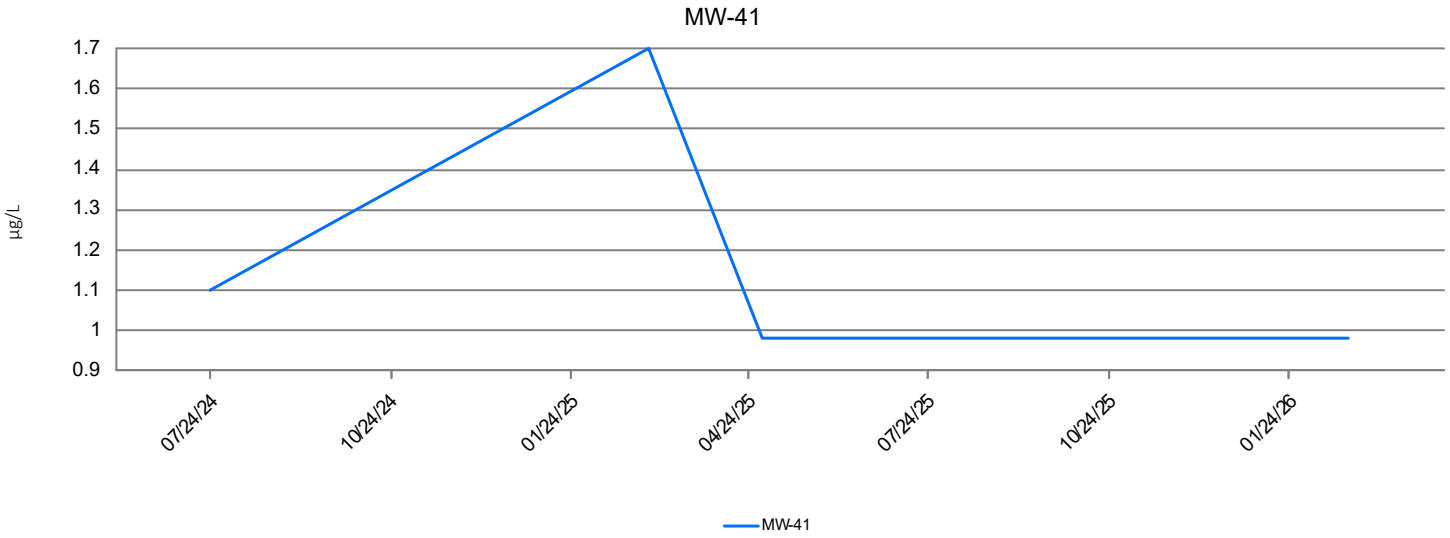
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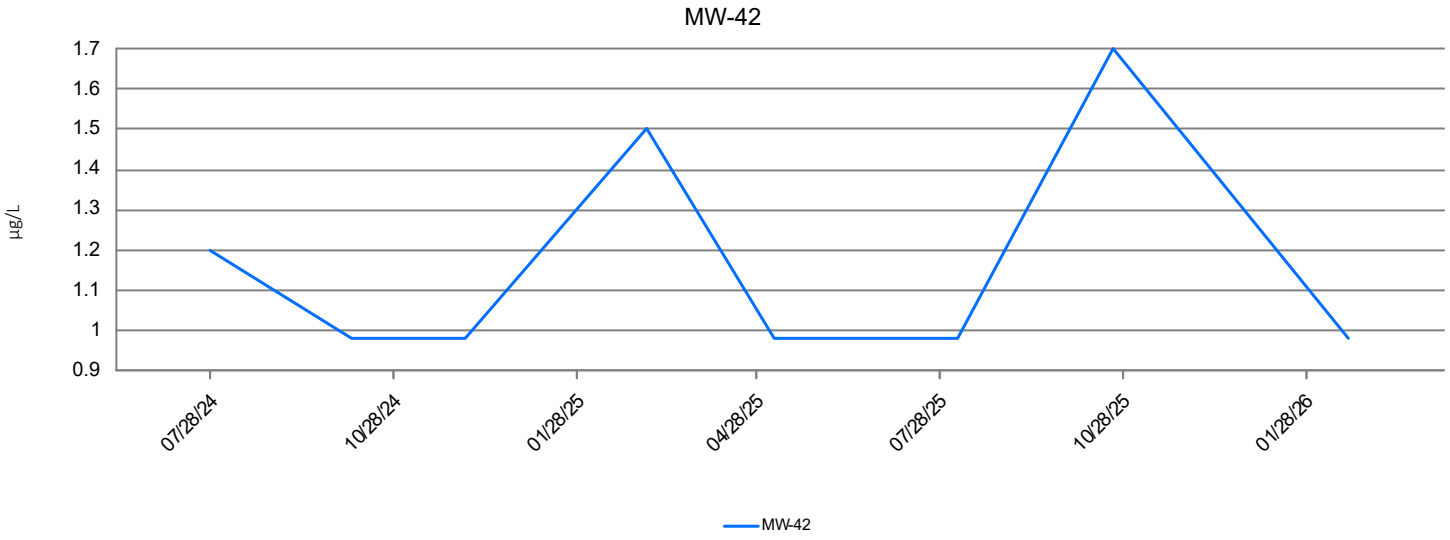
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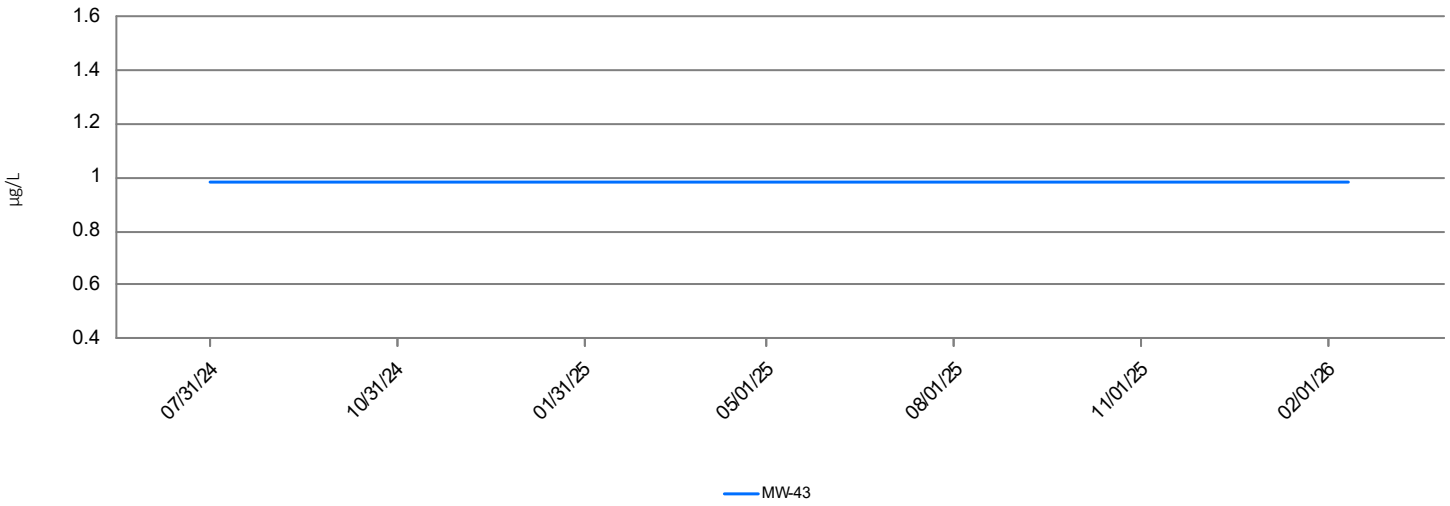
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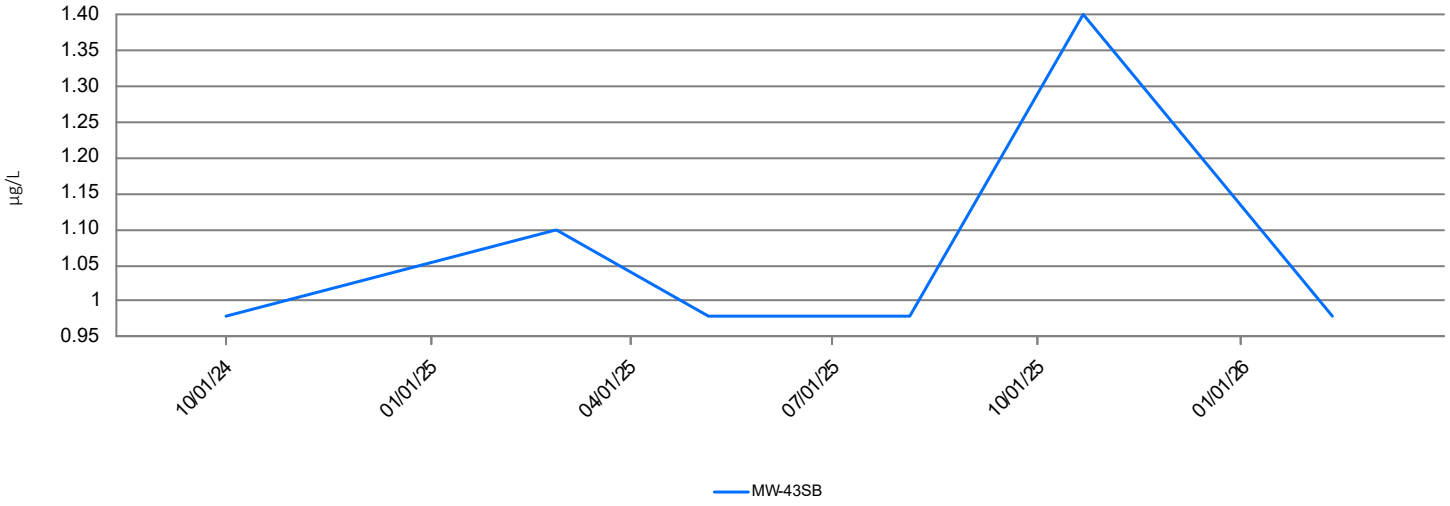
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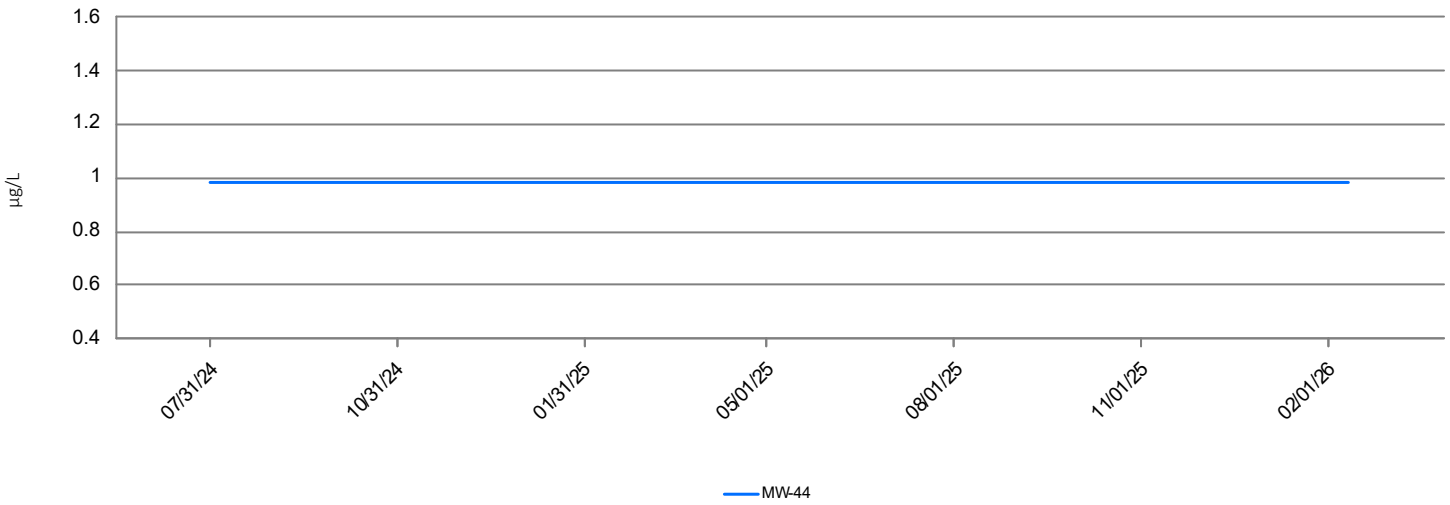
MW-43



MW-43SB



MW-44



Printed Date: 05/21/2026

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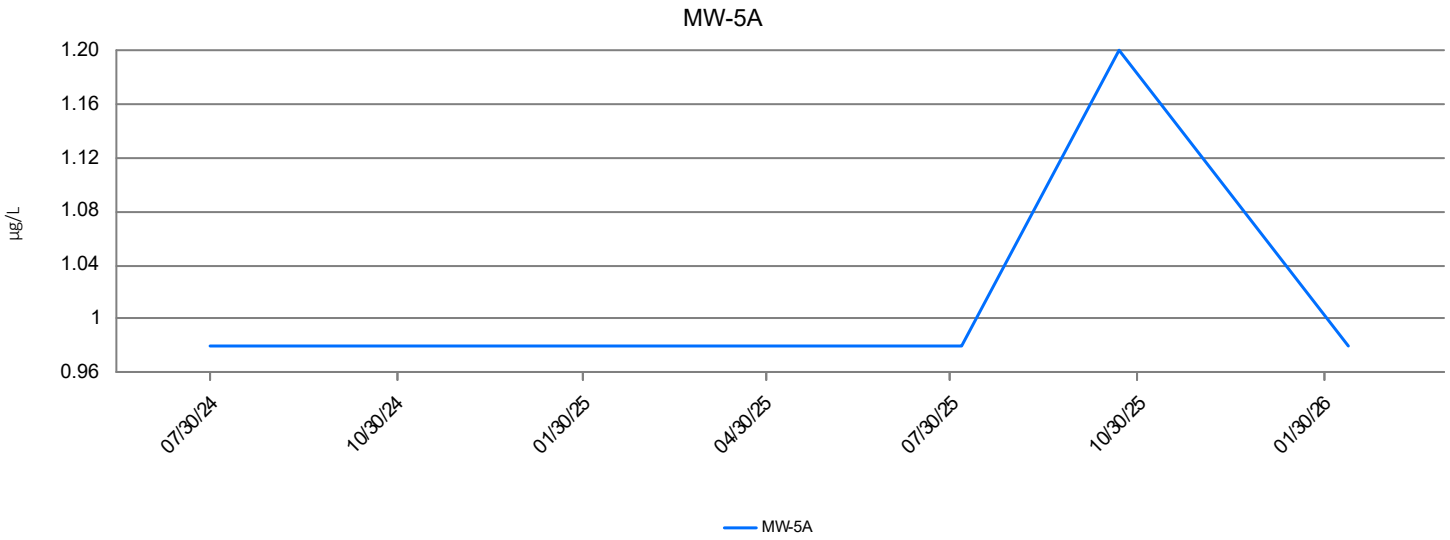
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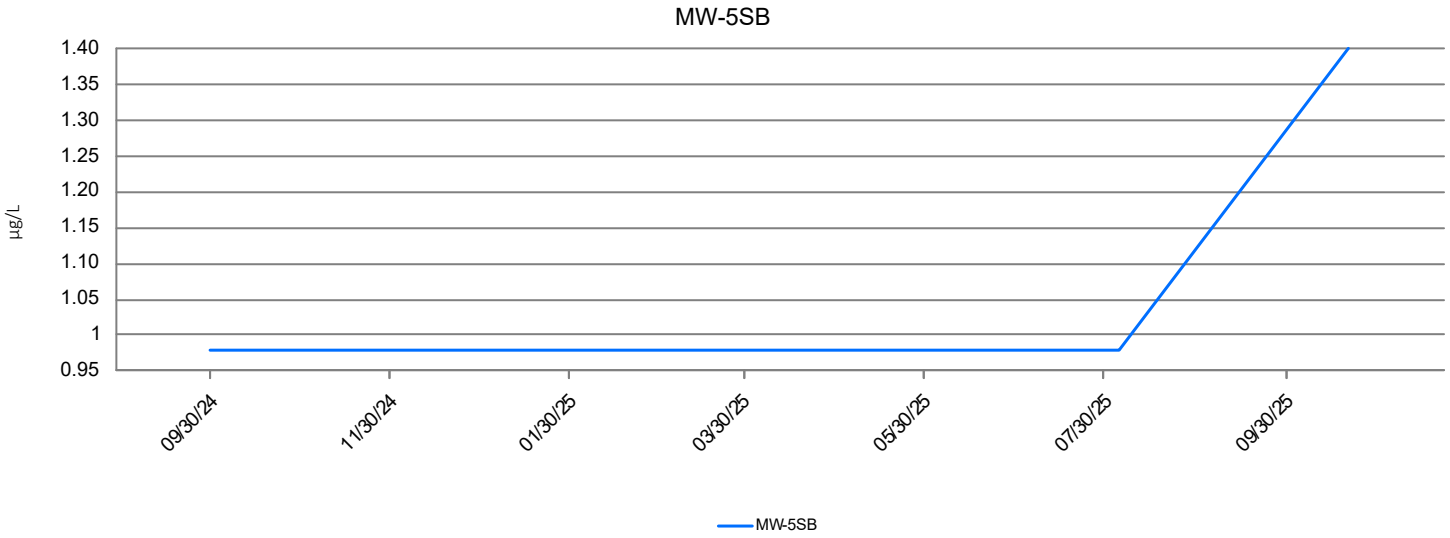
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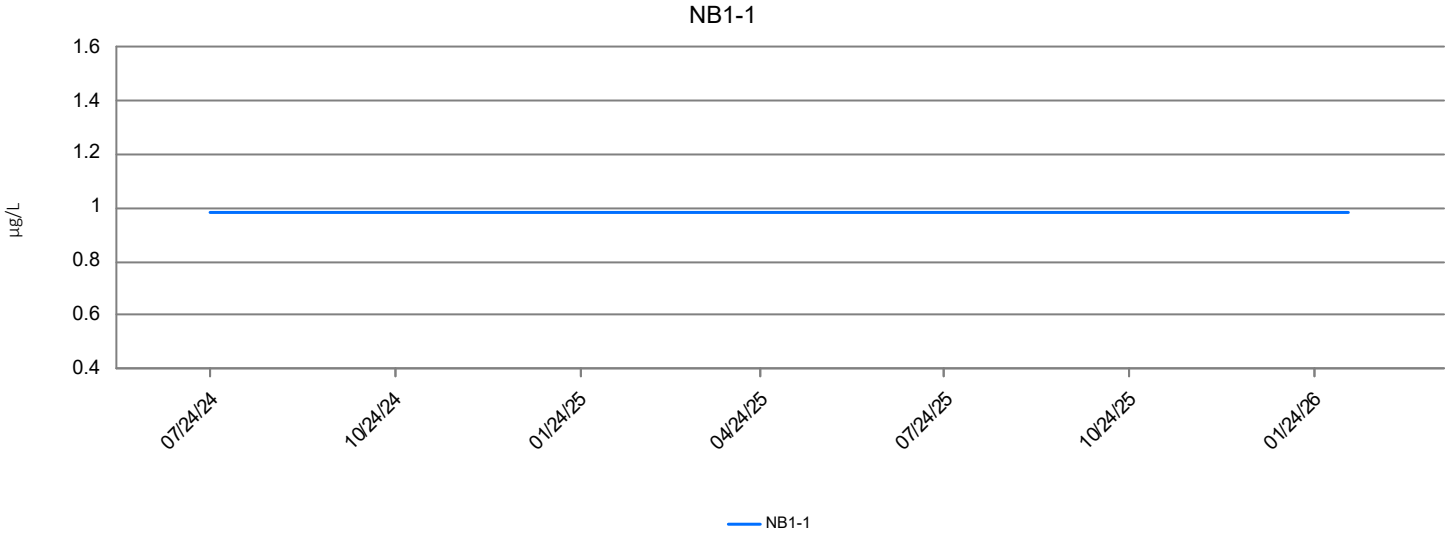
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MonitorPro

No Group Selected, Selenium, Total Recoverable (µg/L)





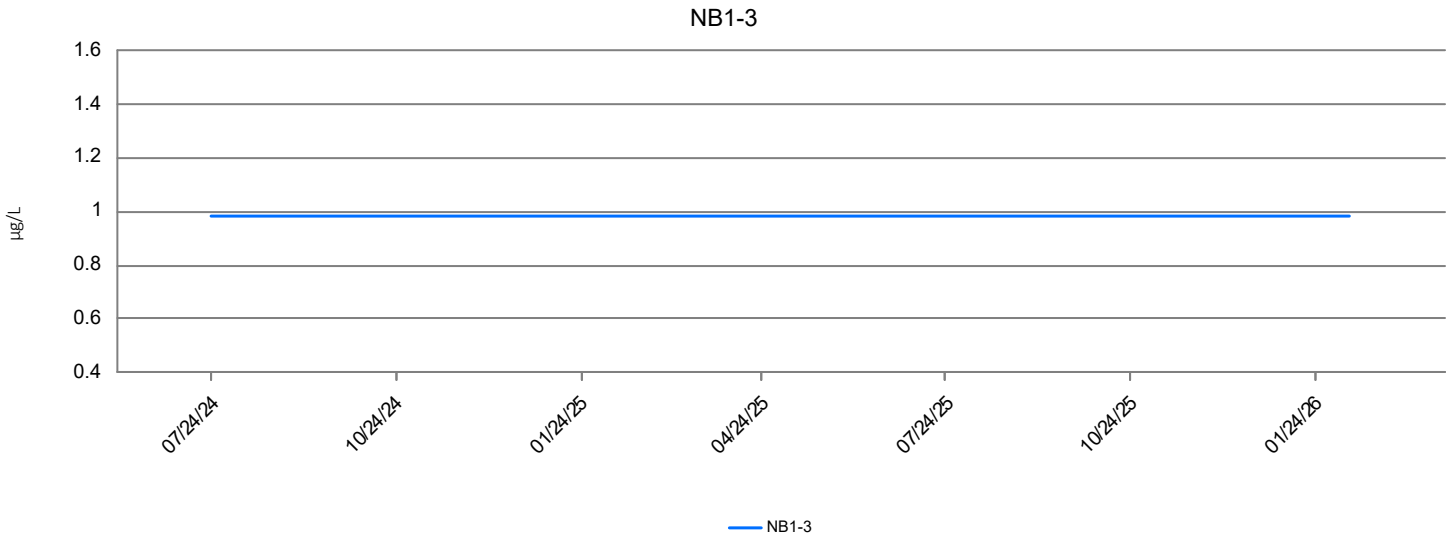


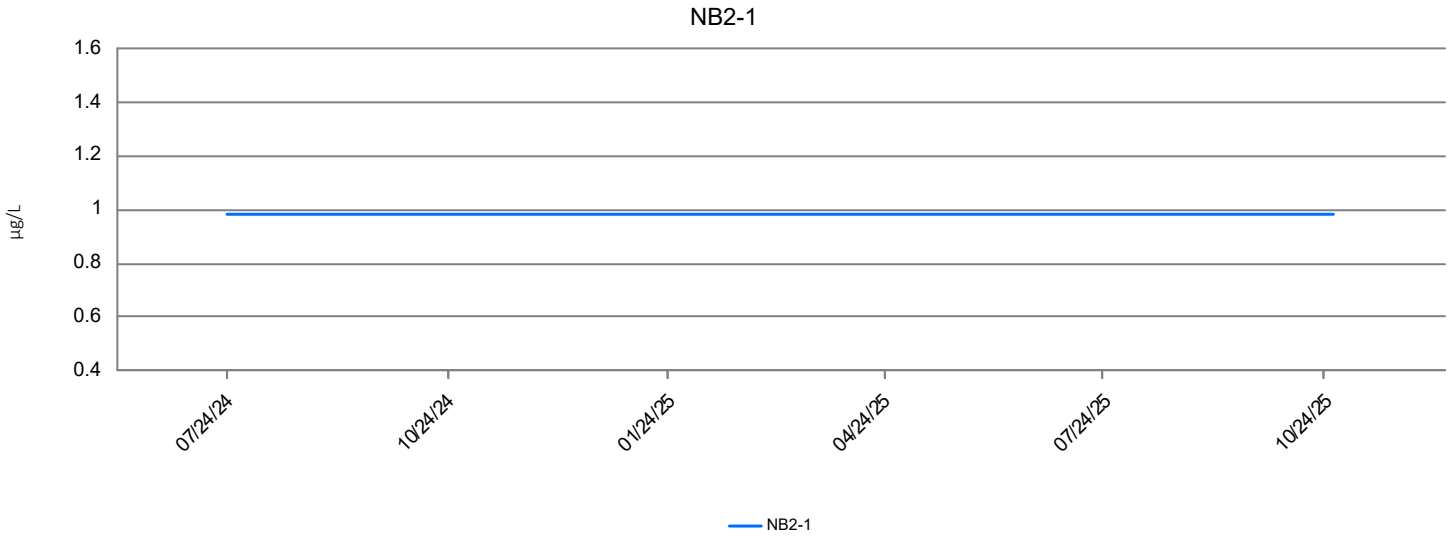
Variable Graphical Report

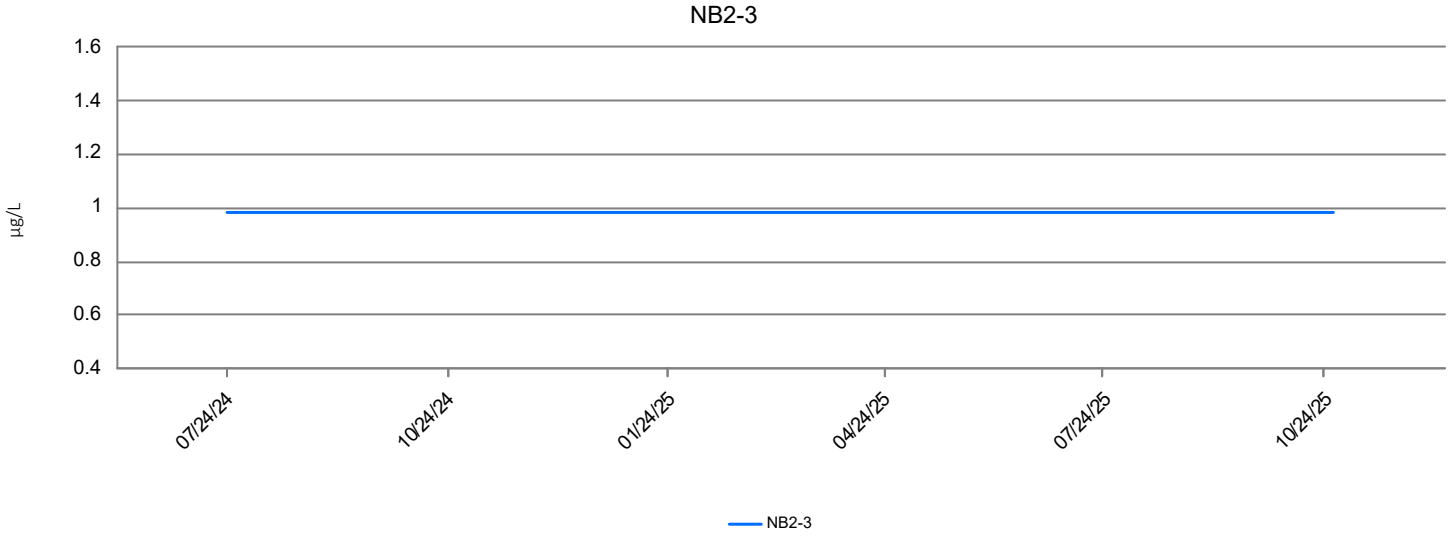
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Selenium, Total Recoverable (µg/L)







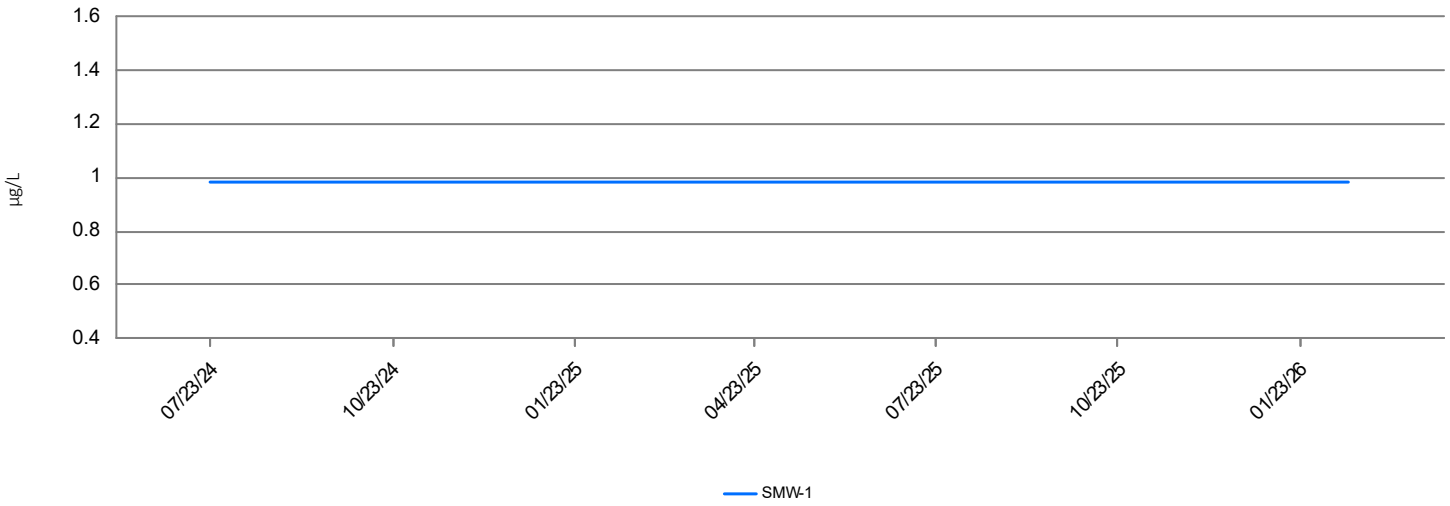
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

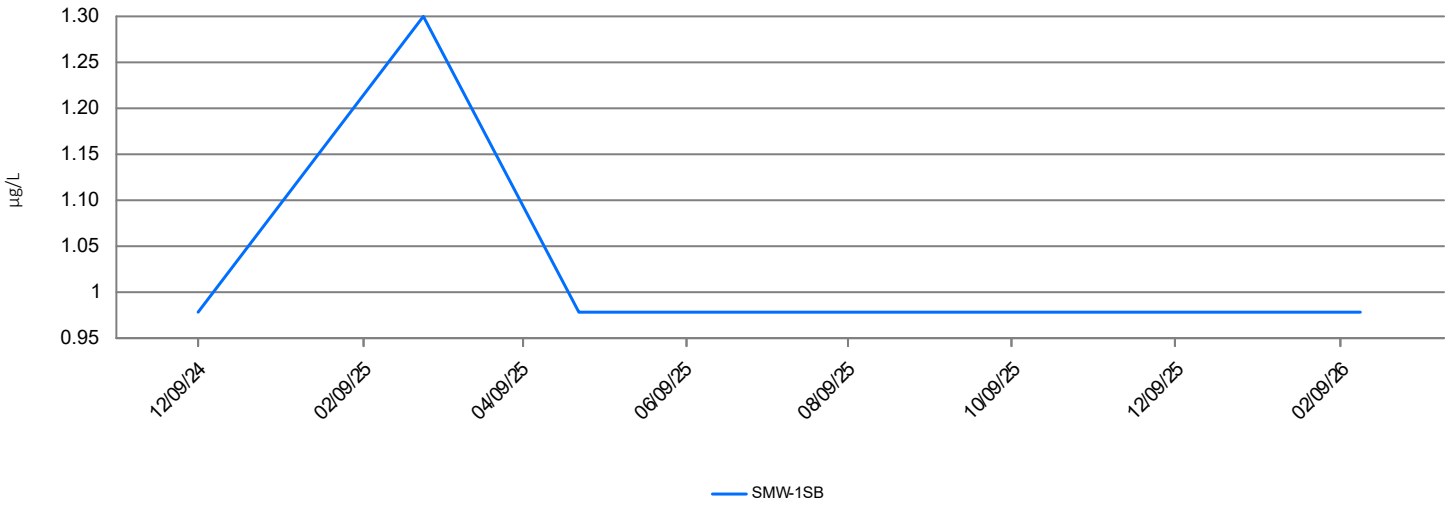
MonitorPro

No Group Selected, Selenium, Total Recoverable (µg/L)

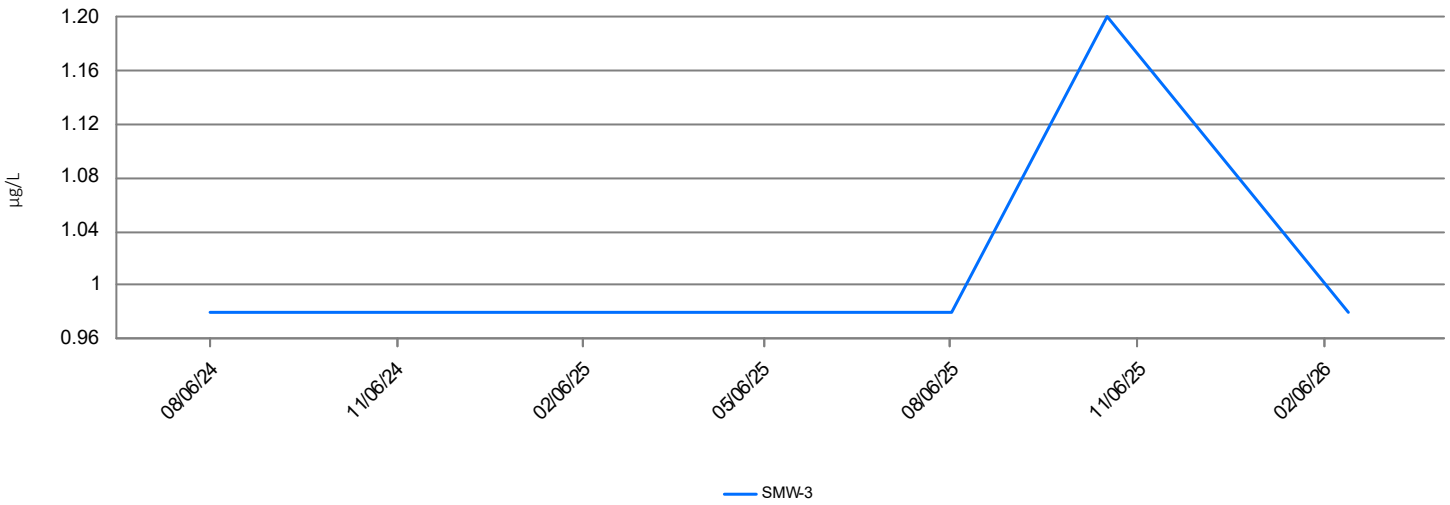
SMW-1



SMW-1SB



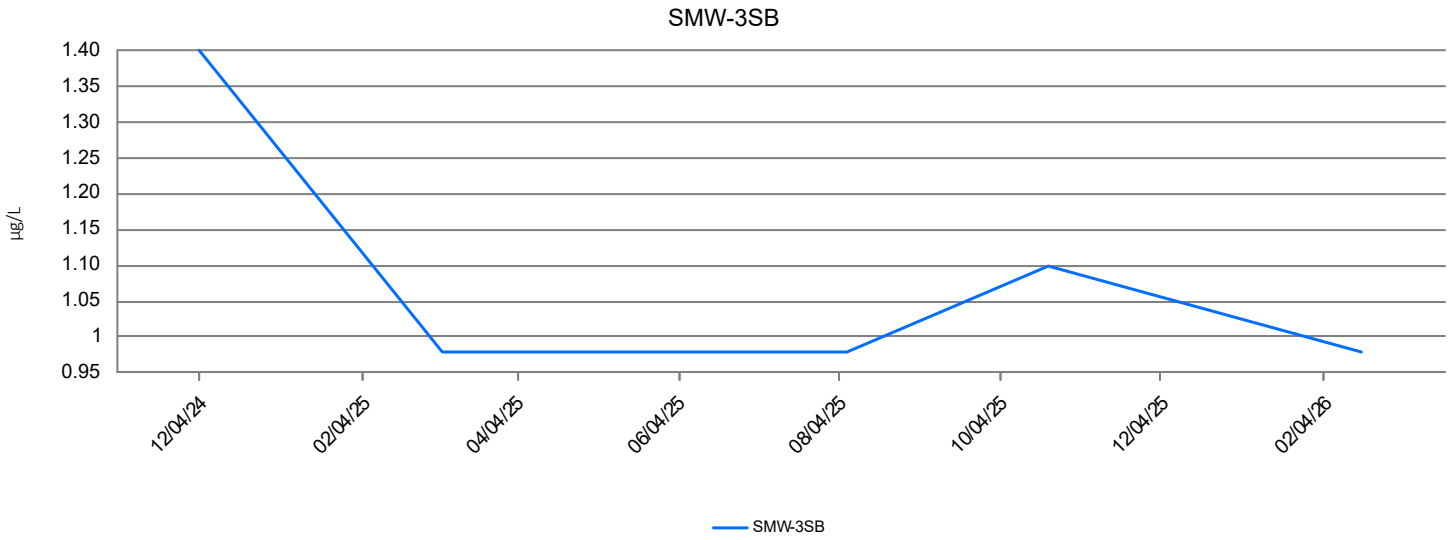
SMW-3



Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

No Group Selected, Selenium, Total Recoverable (µg/L)

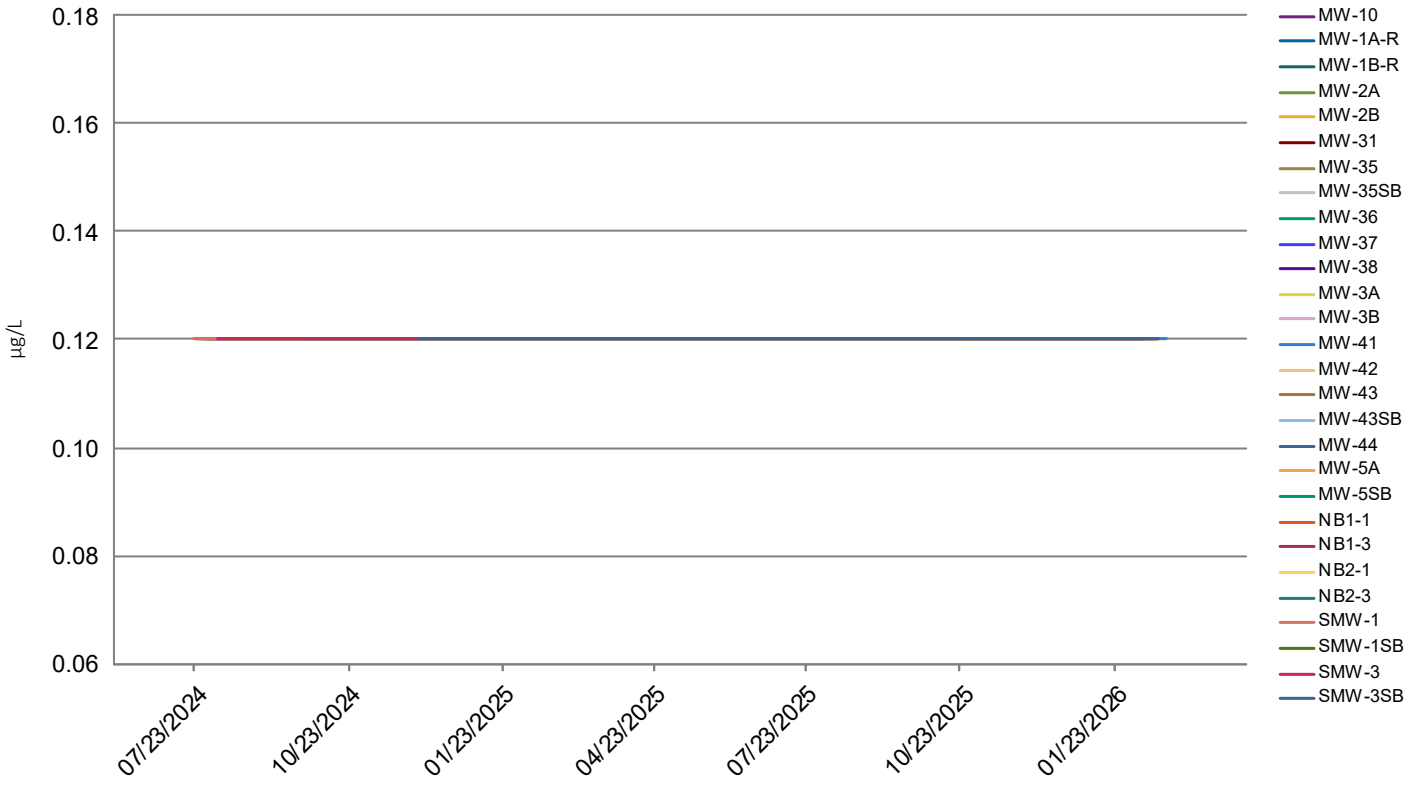


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Silver, Dissolved (µg/L)

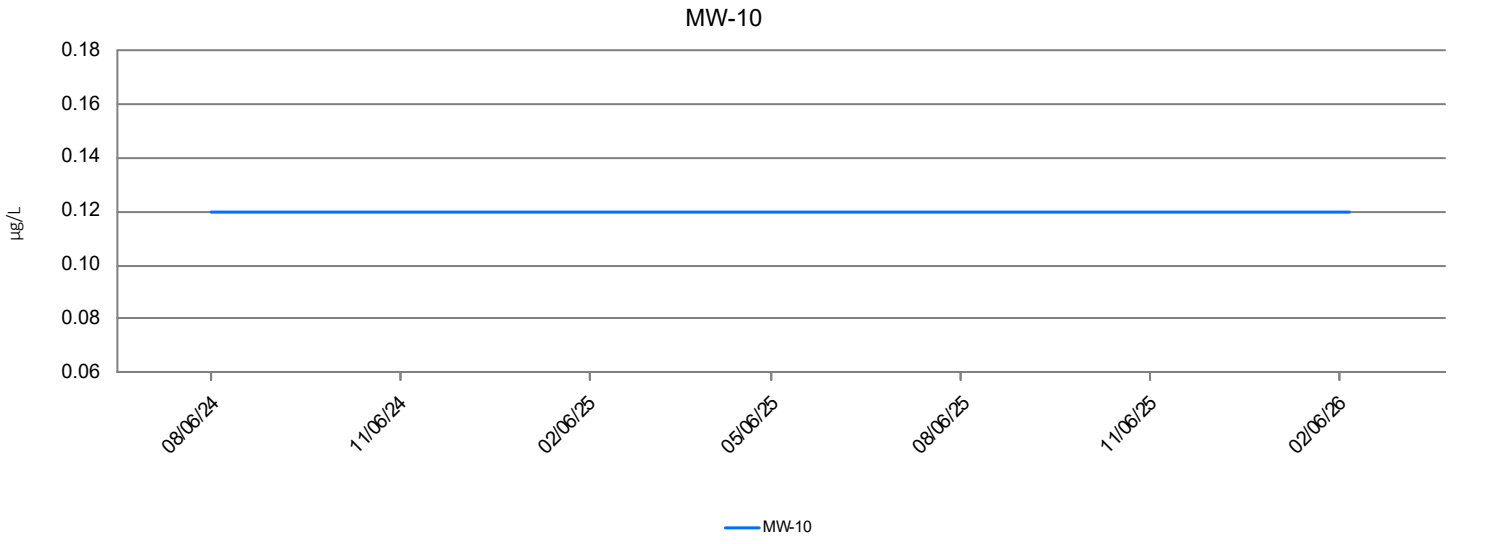


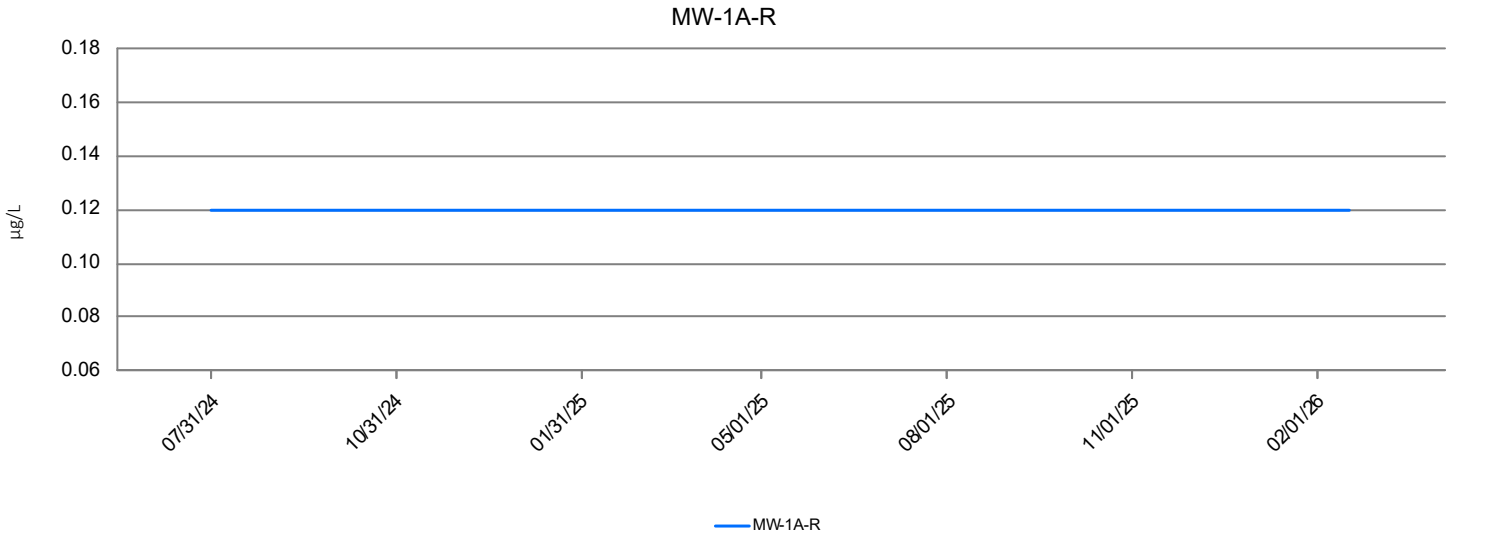
Variable Graphical Report

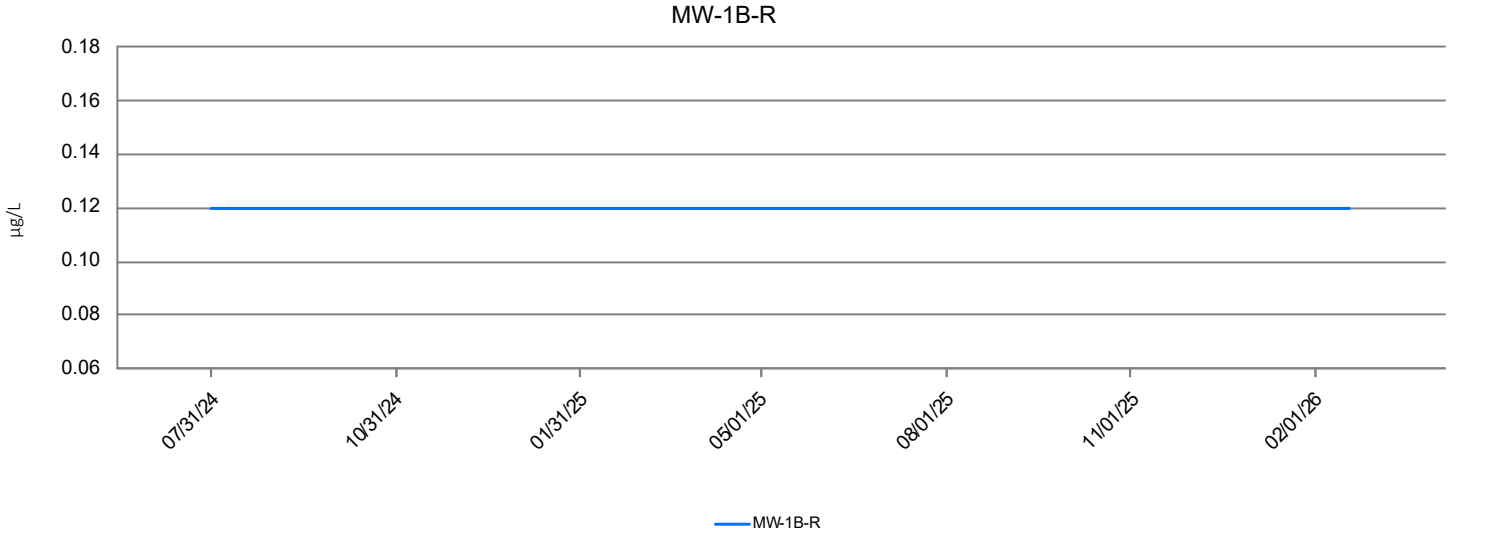
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Silver, Dissolved (µg/L)







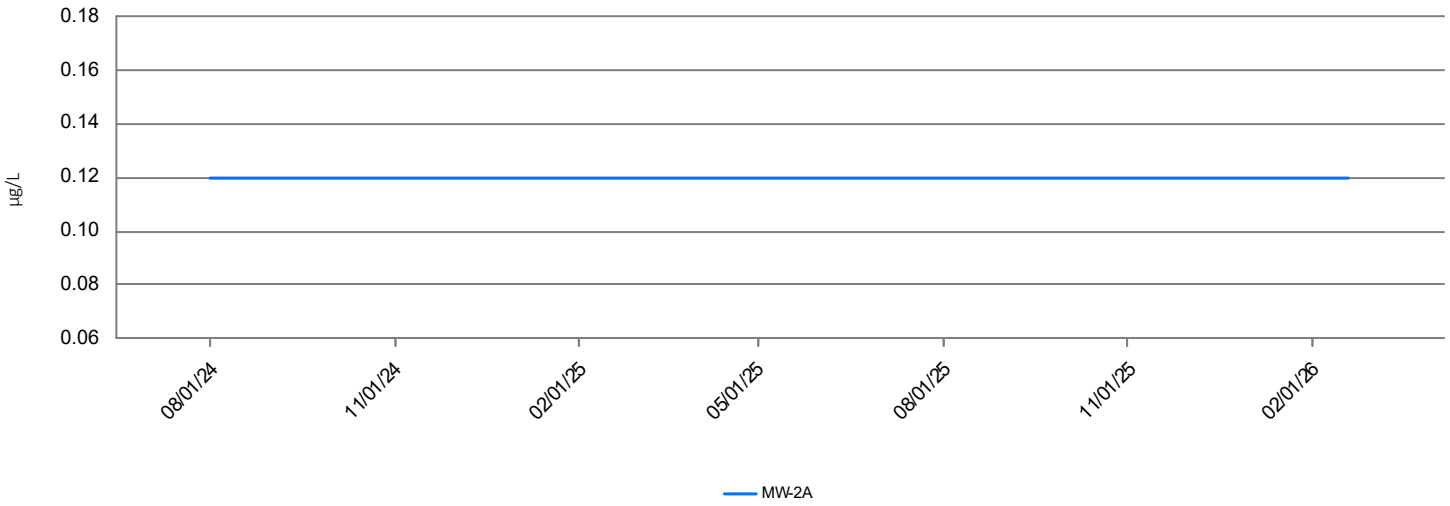
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

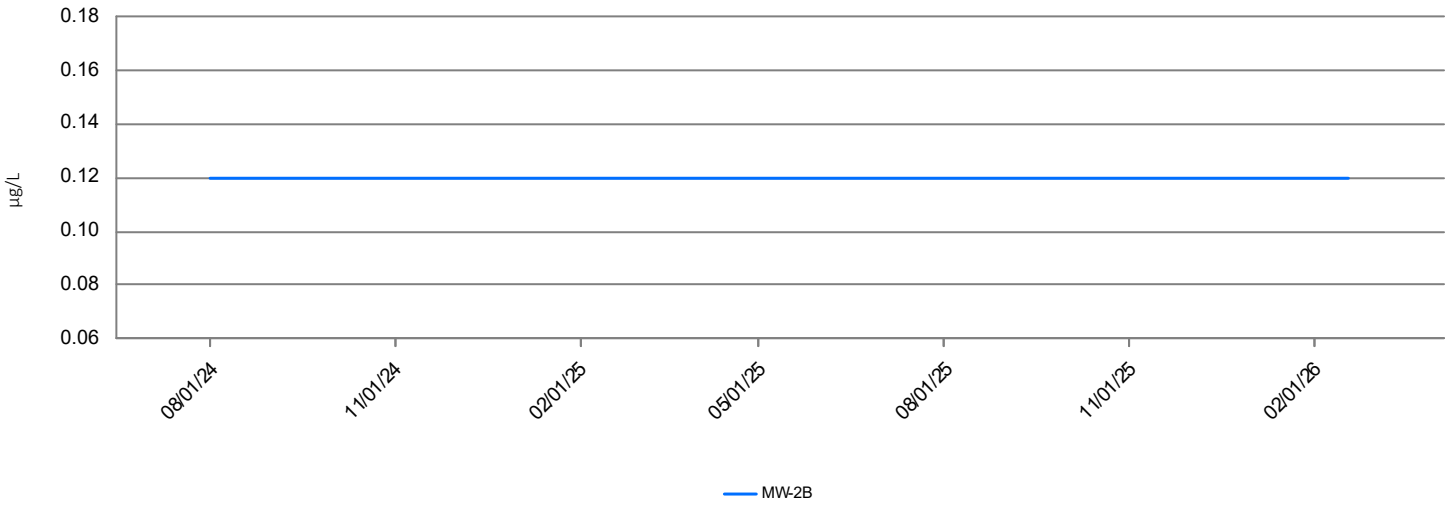
MonitorPro

No Group Selected, Silver, Dissolved (µg/L)

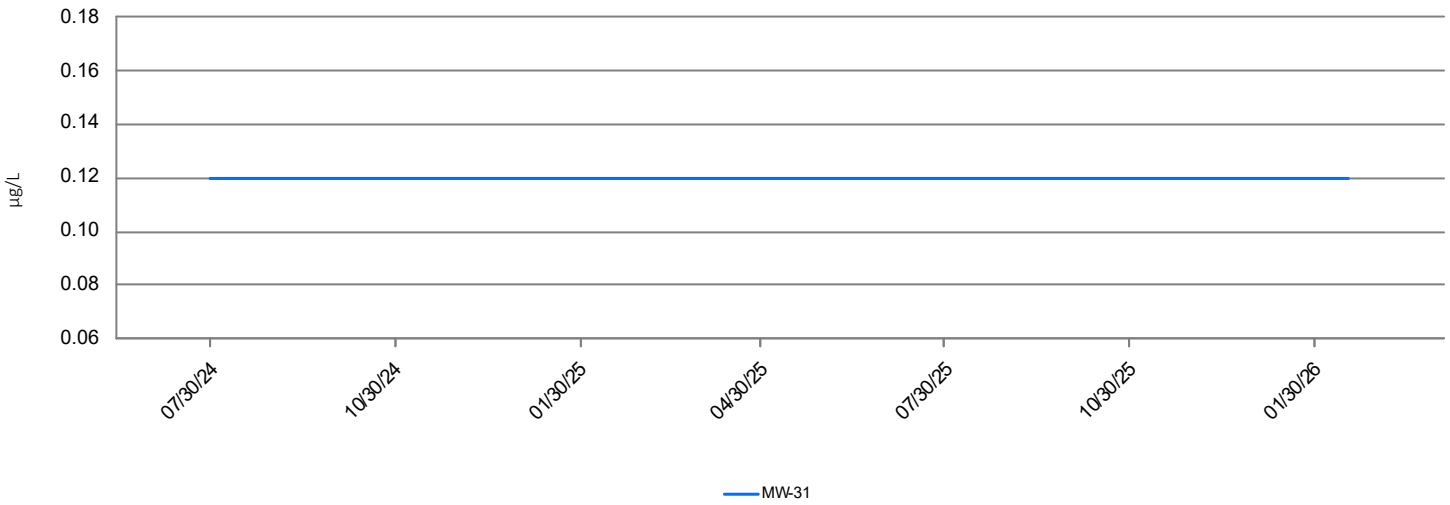
MW-2A



MW-2B



MW-31

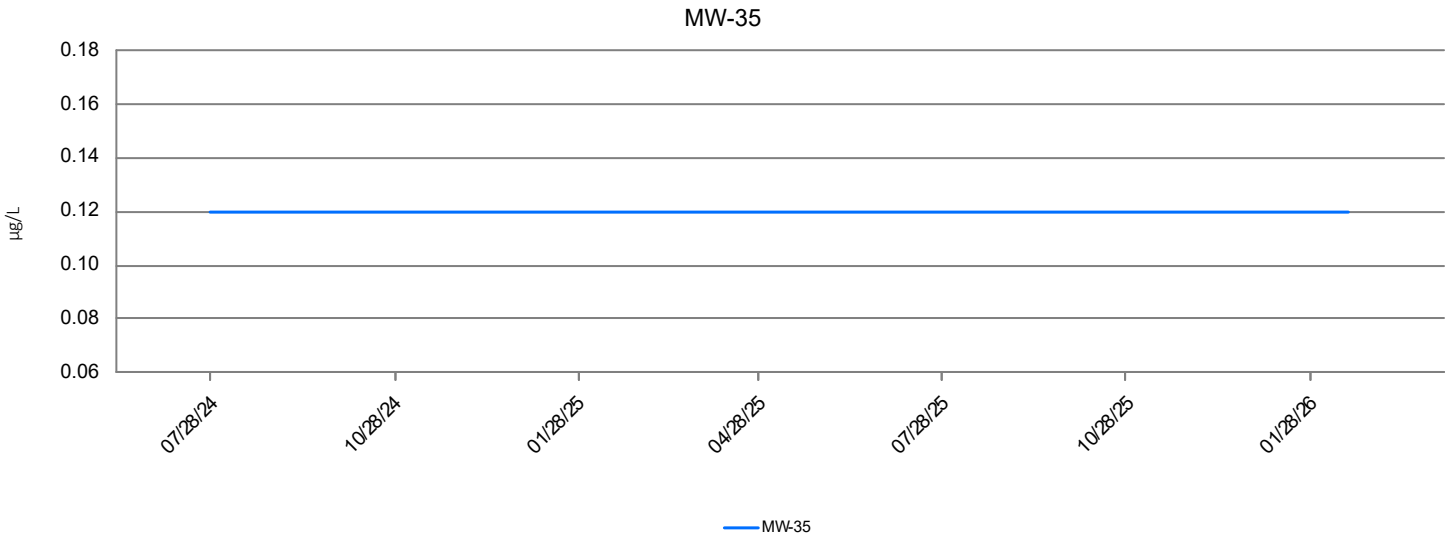


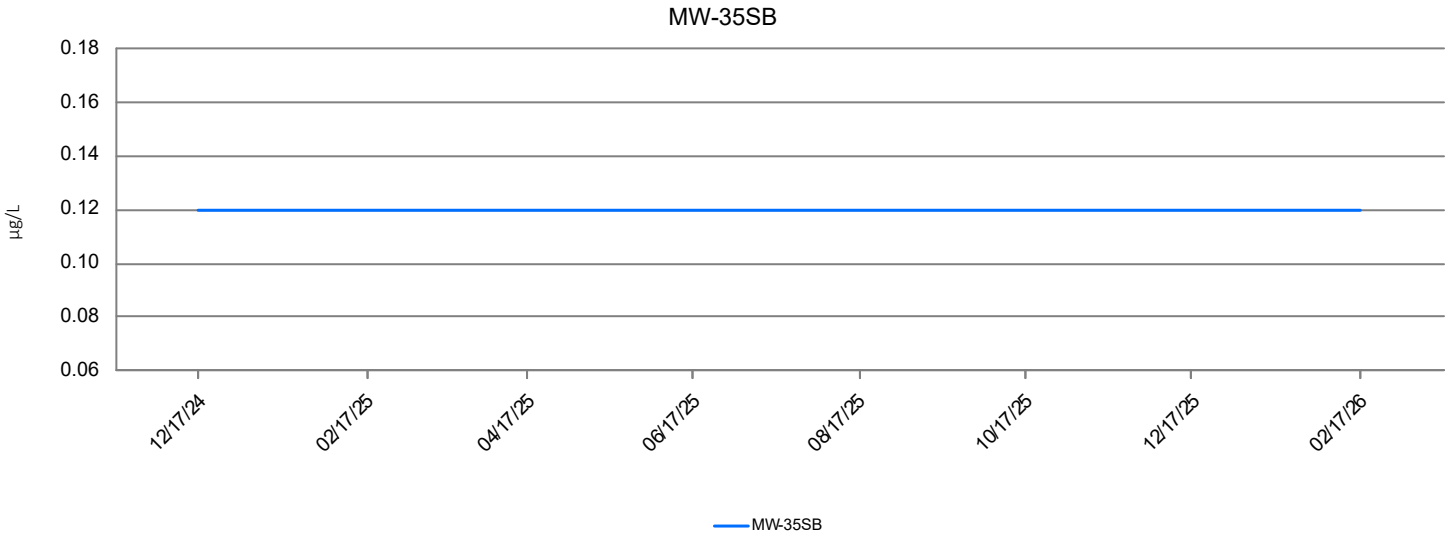
Variable Graphical Report

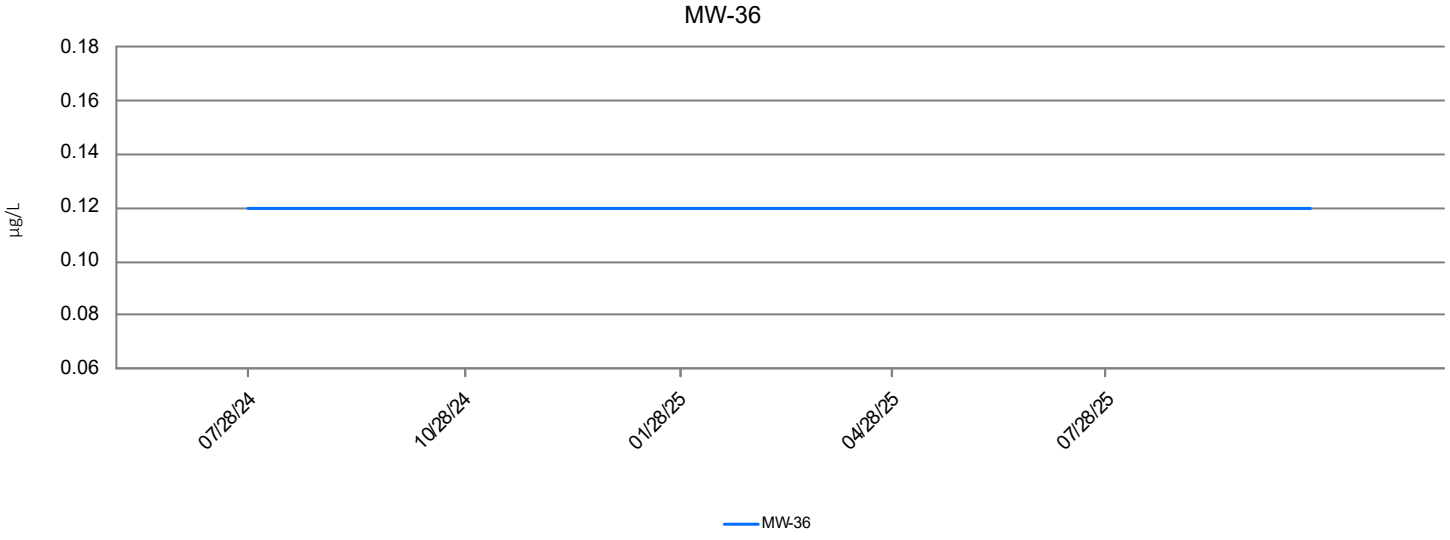
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Silver, Dissolved (µg/L)





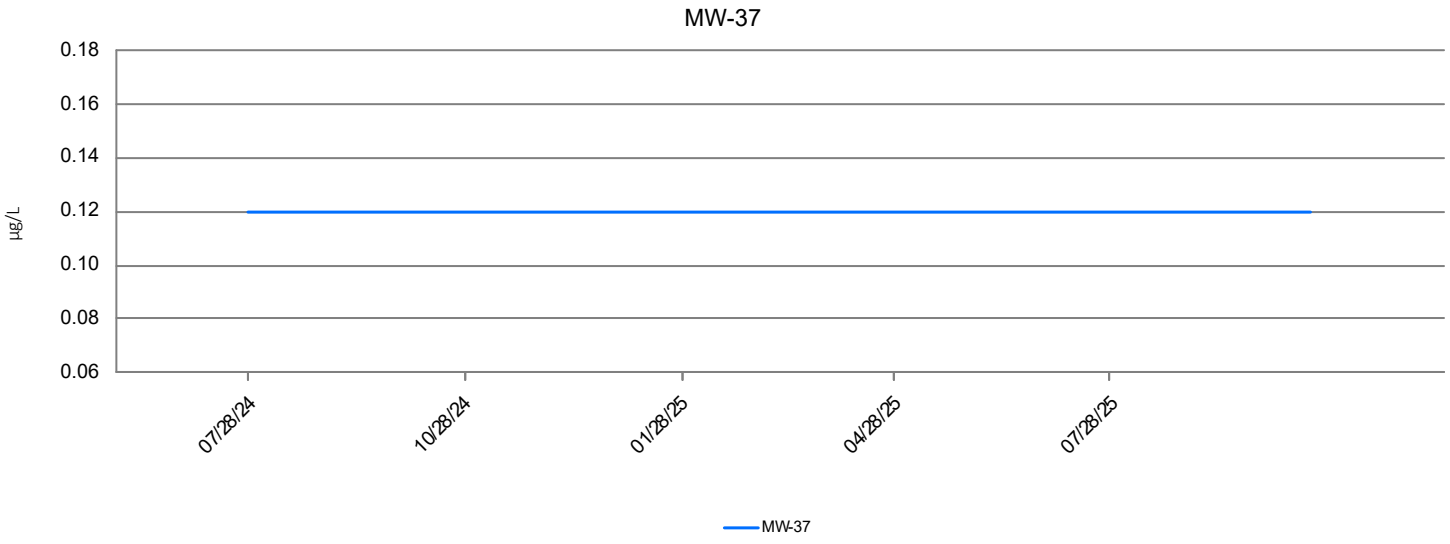


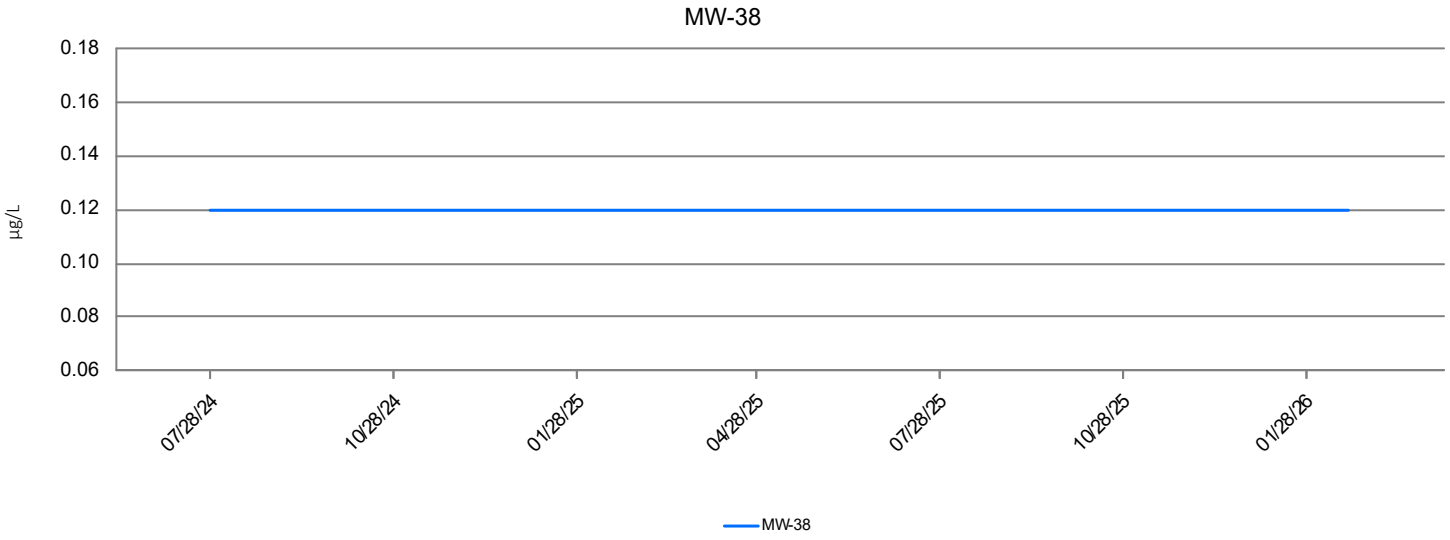
Variable Graphical Report

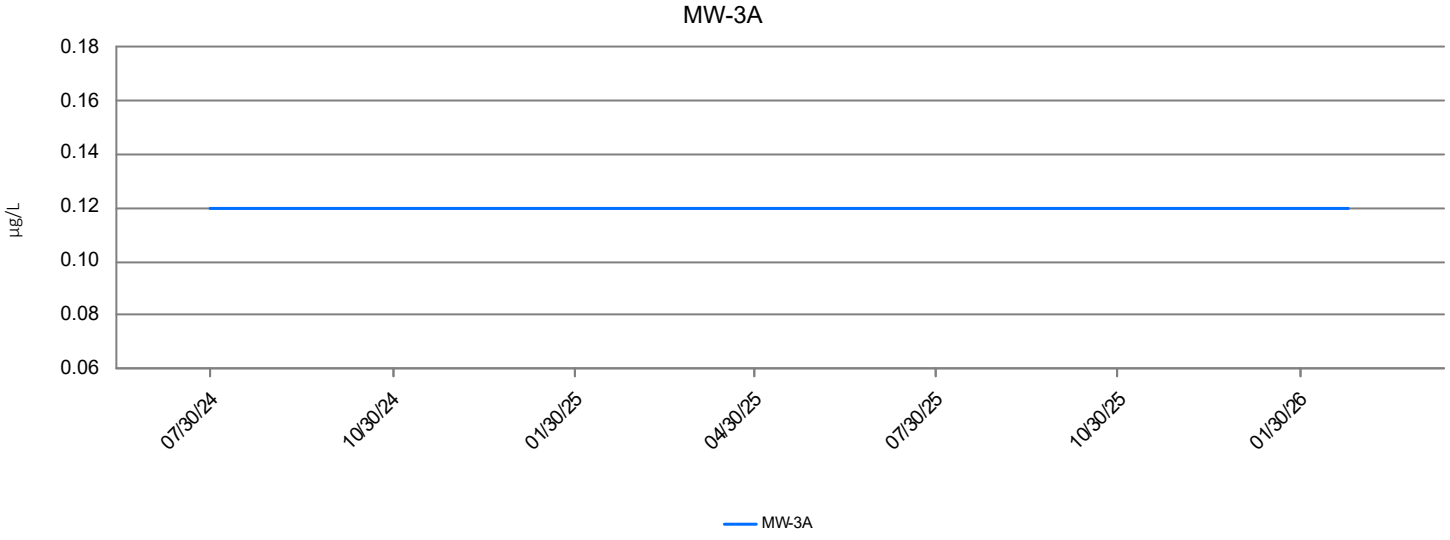
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Silver, Dissolved (µg/L)





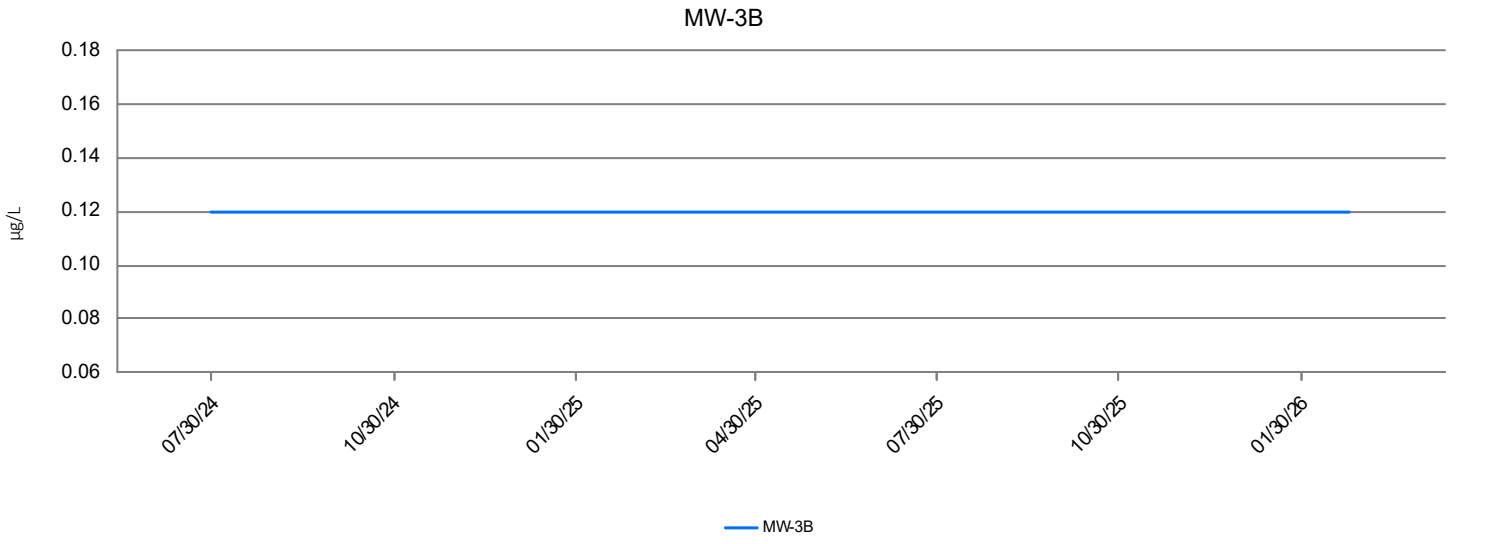


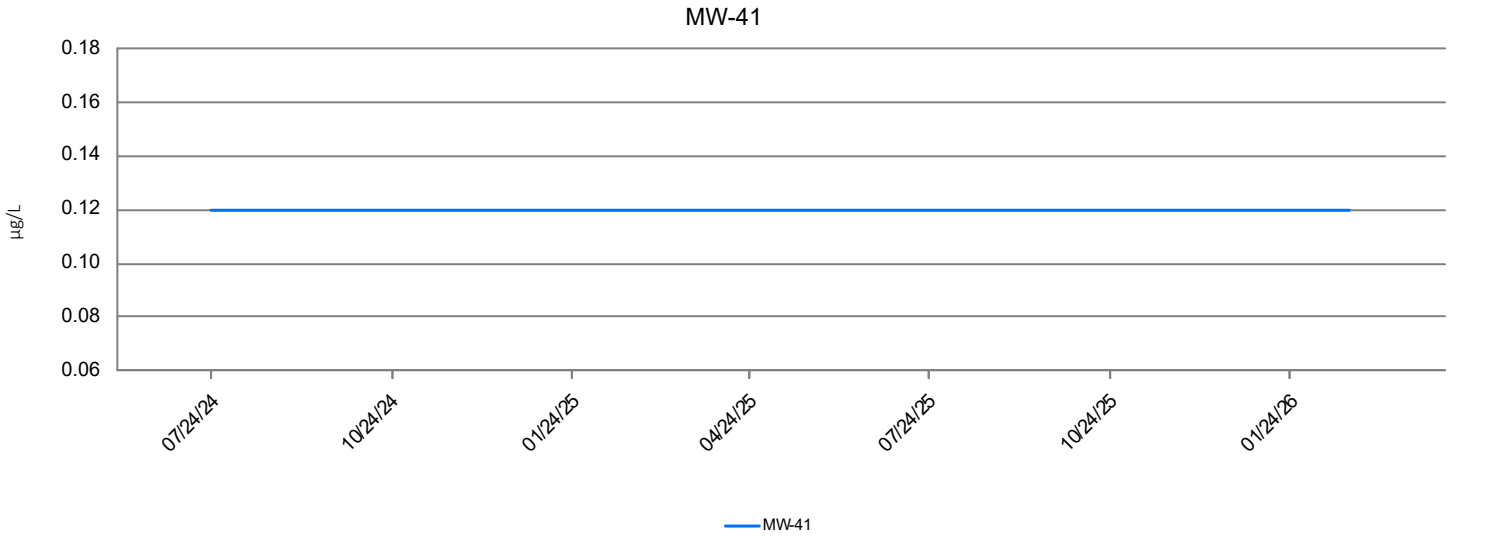
Variable Graphical Report

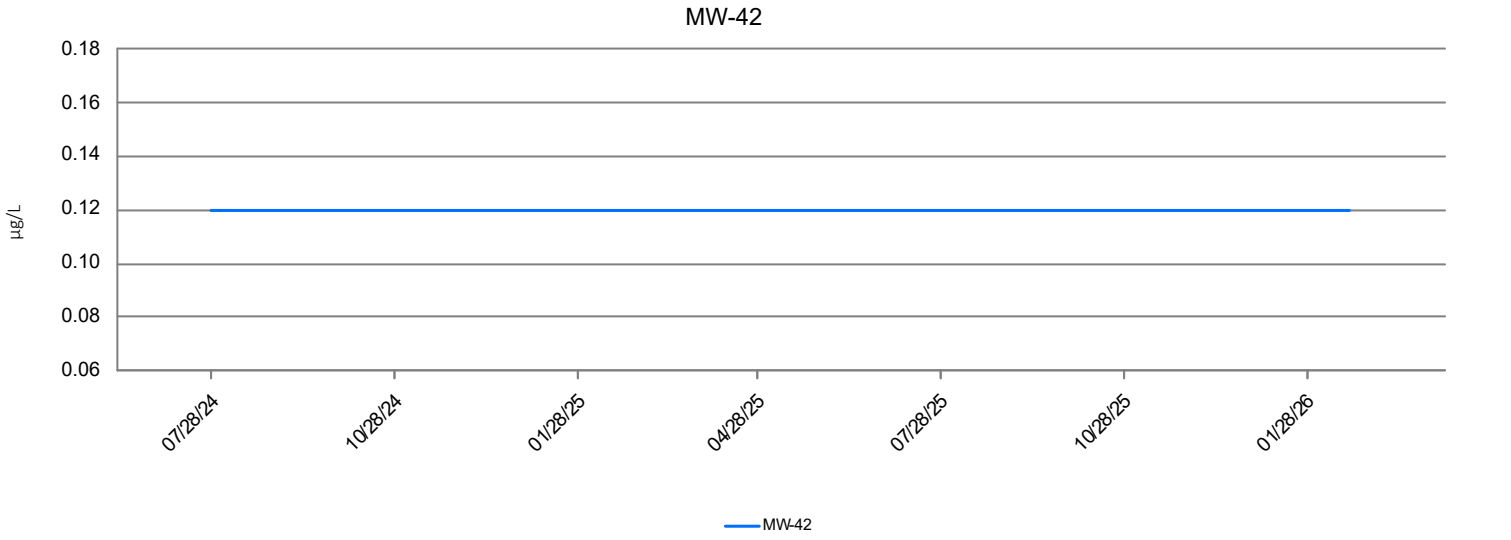
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Silver, Dissolved (µg/L)







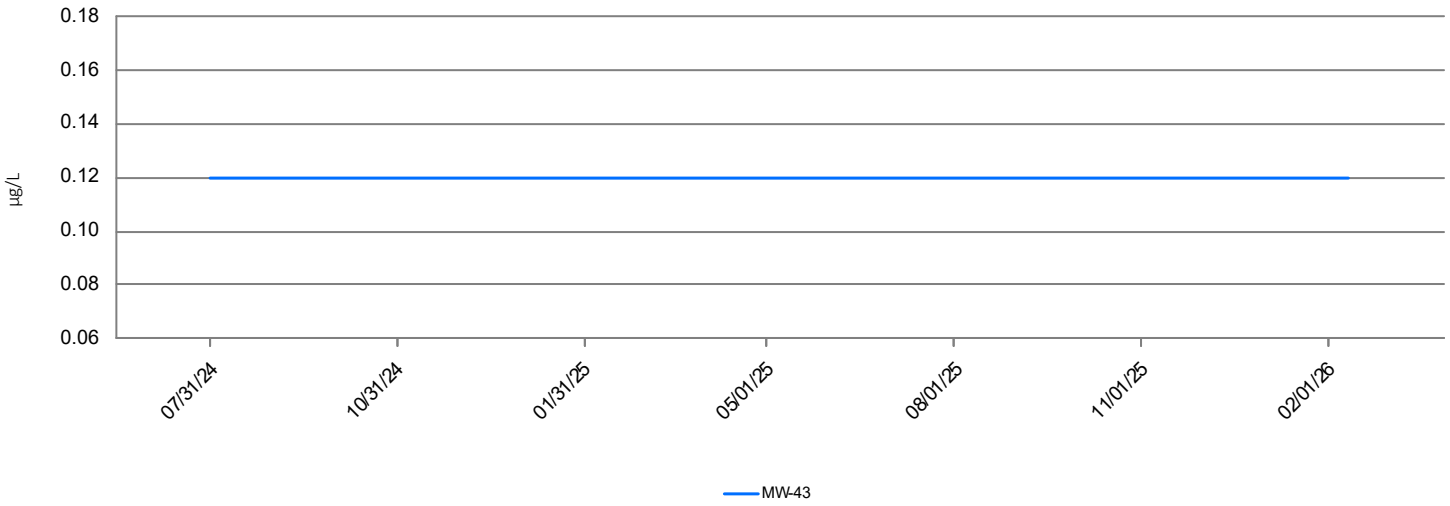
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

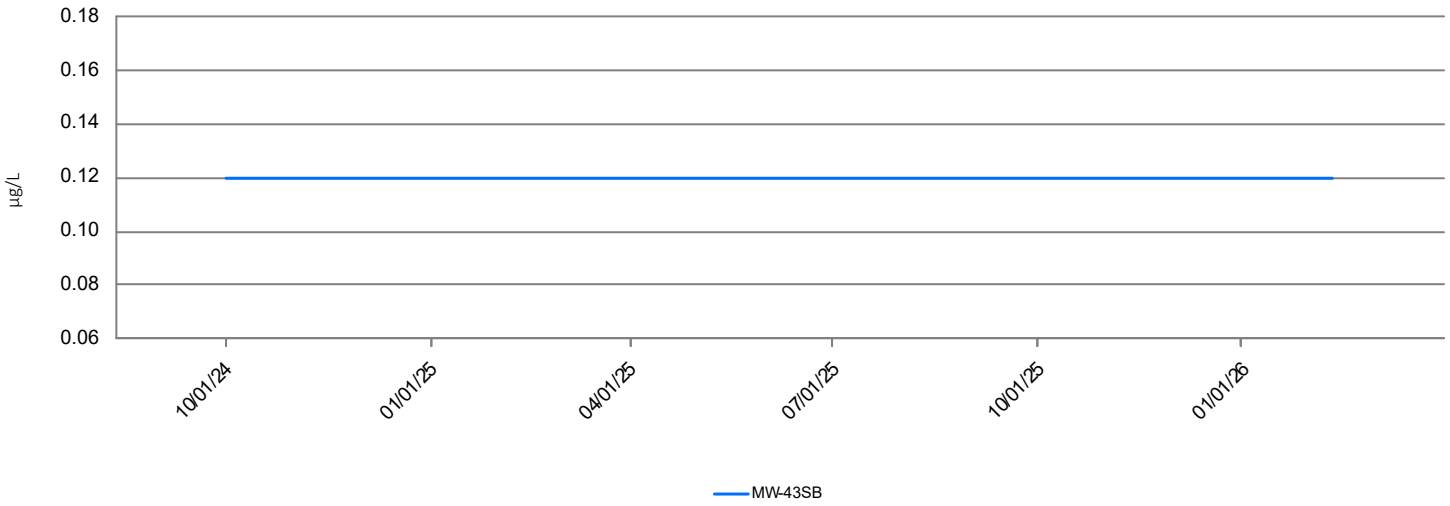
MonitorPro

No Group Selected, Silver, Dissolved (µg/L)

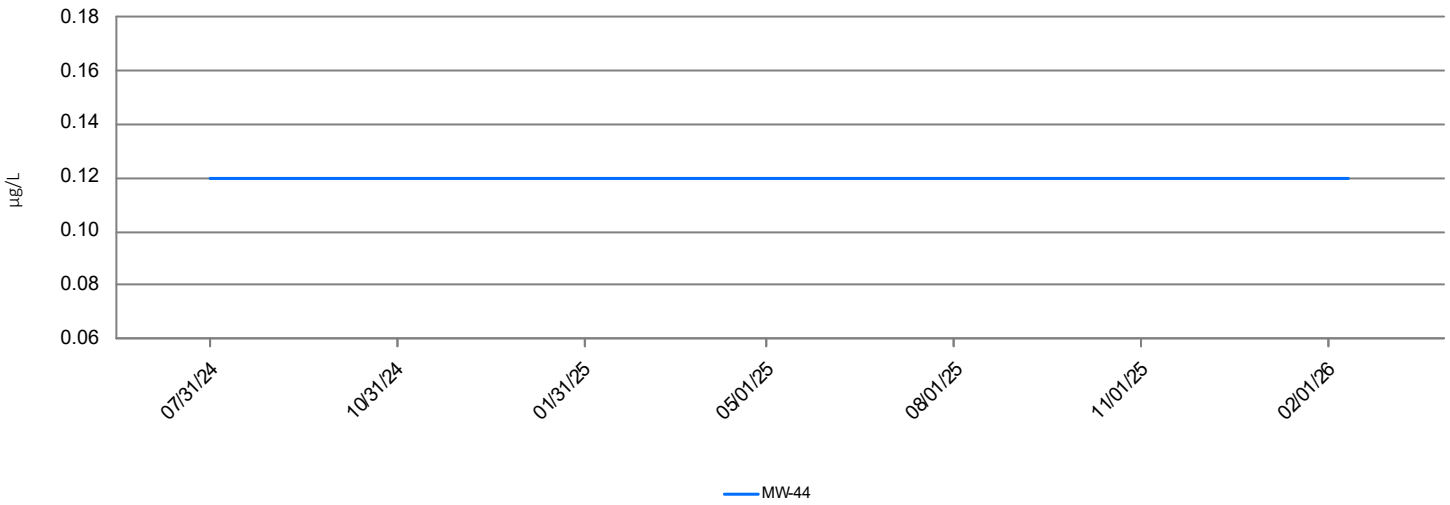
MW-43



MW-43SB



MW-44

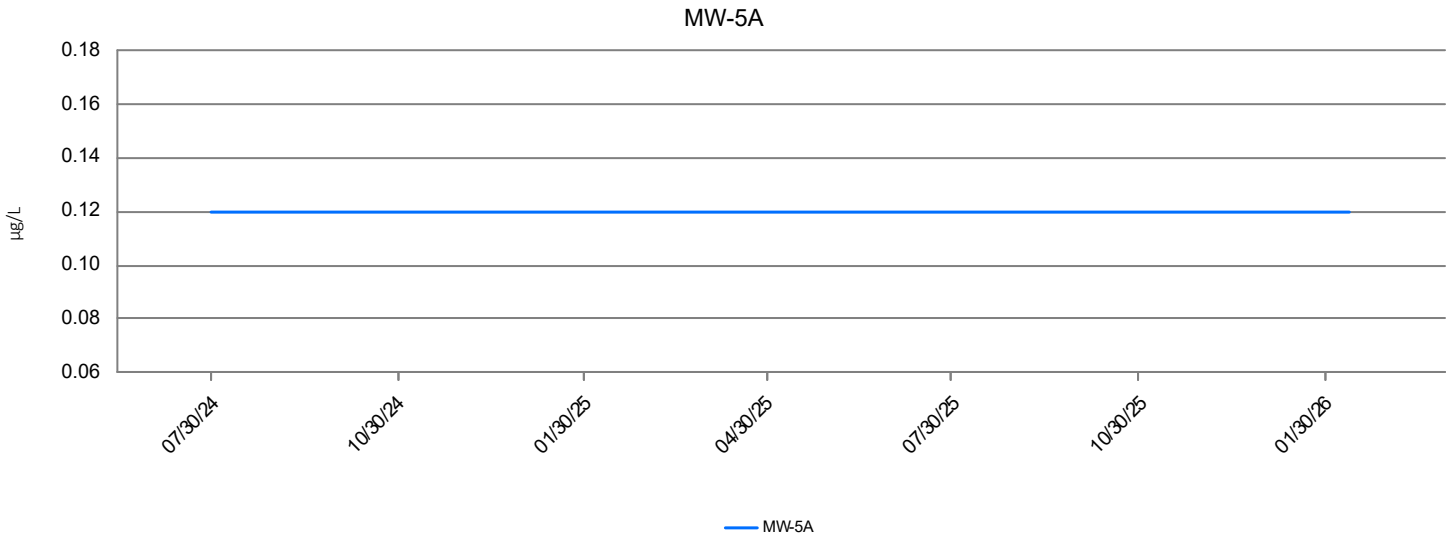


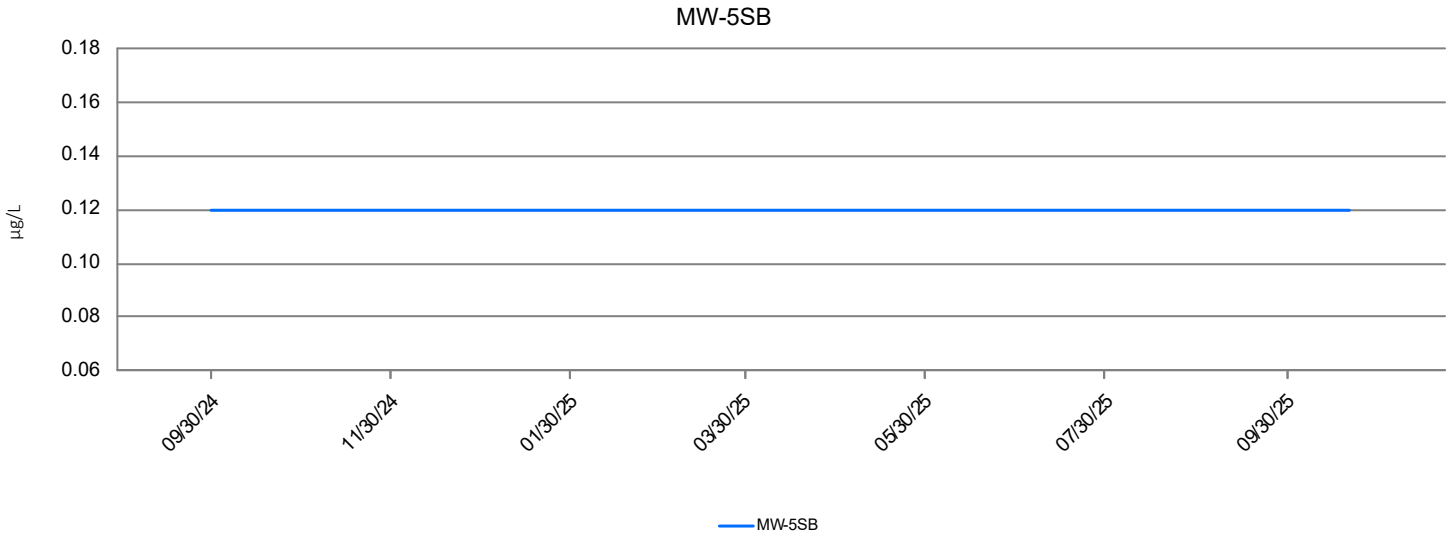
Variable Graphical Report

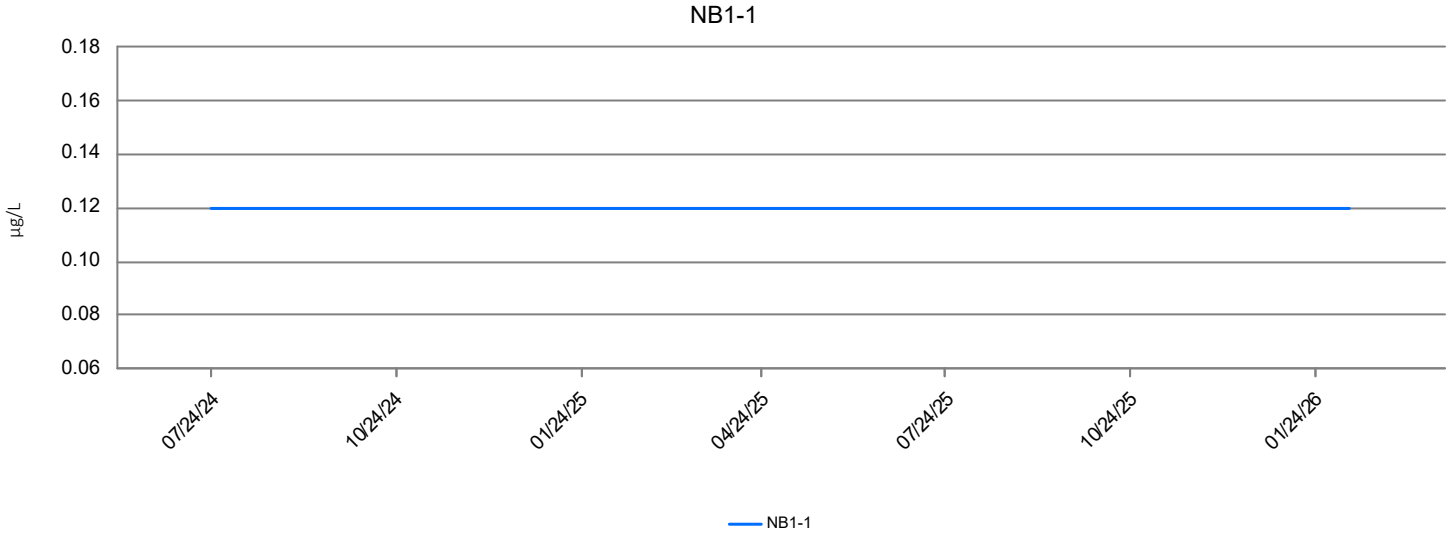
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Silver, Dissolved (µg/L)





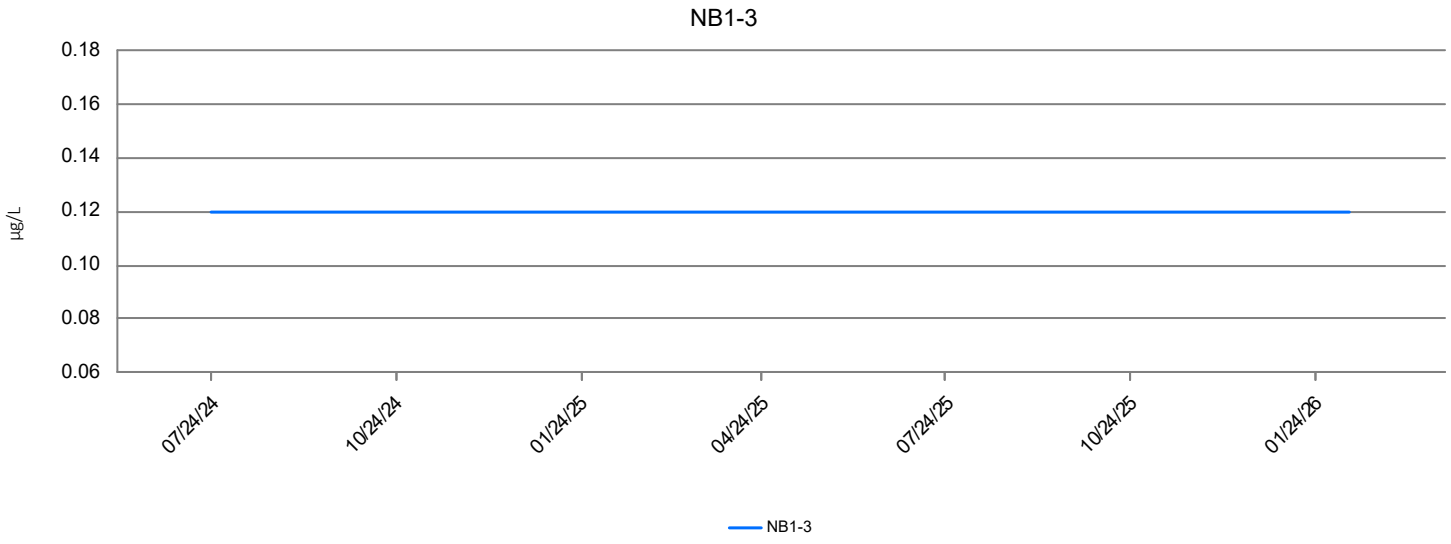


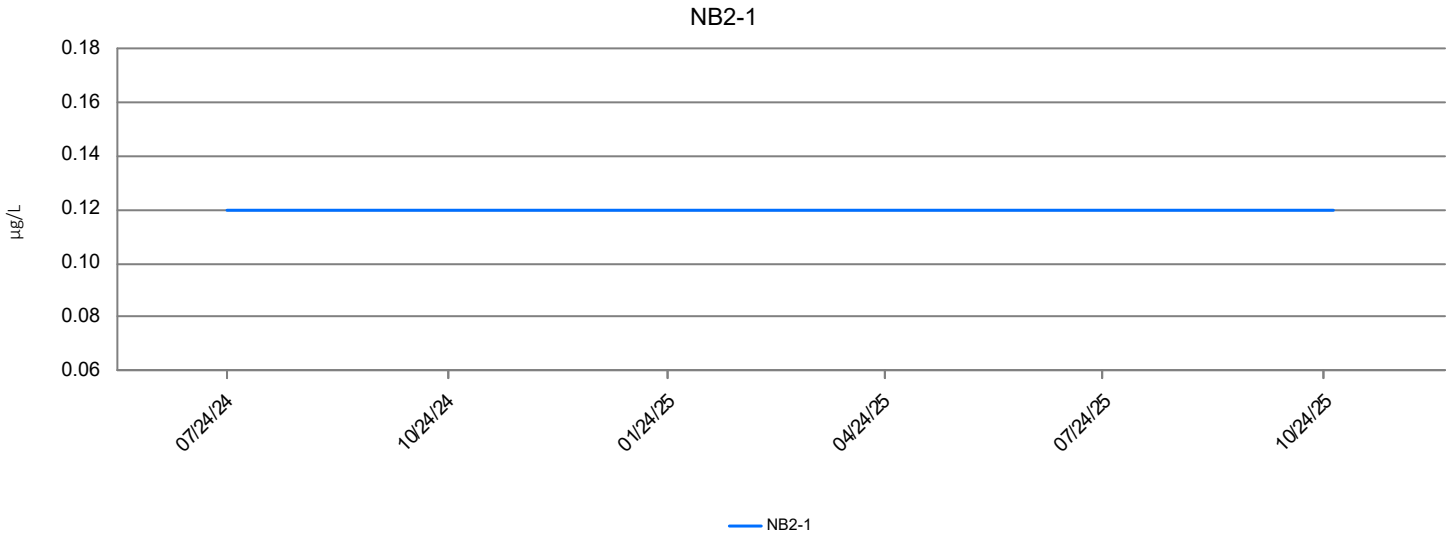
Variable Graphical Report

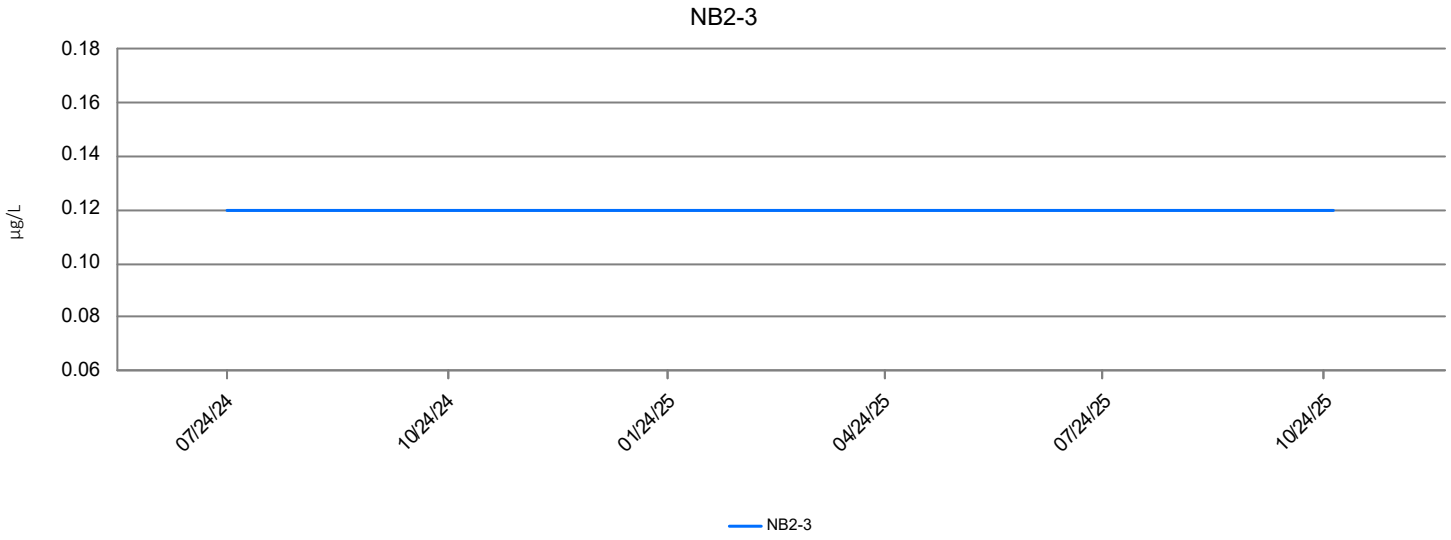
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Silver, Dissolved (µg/L)







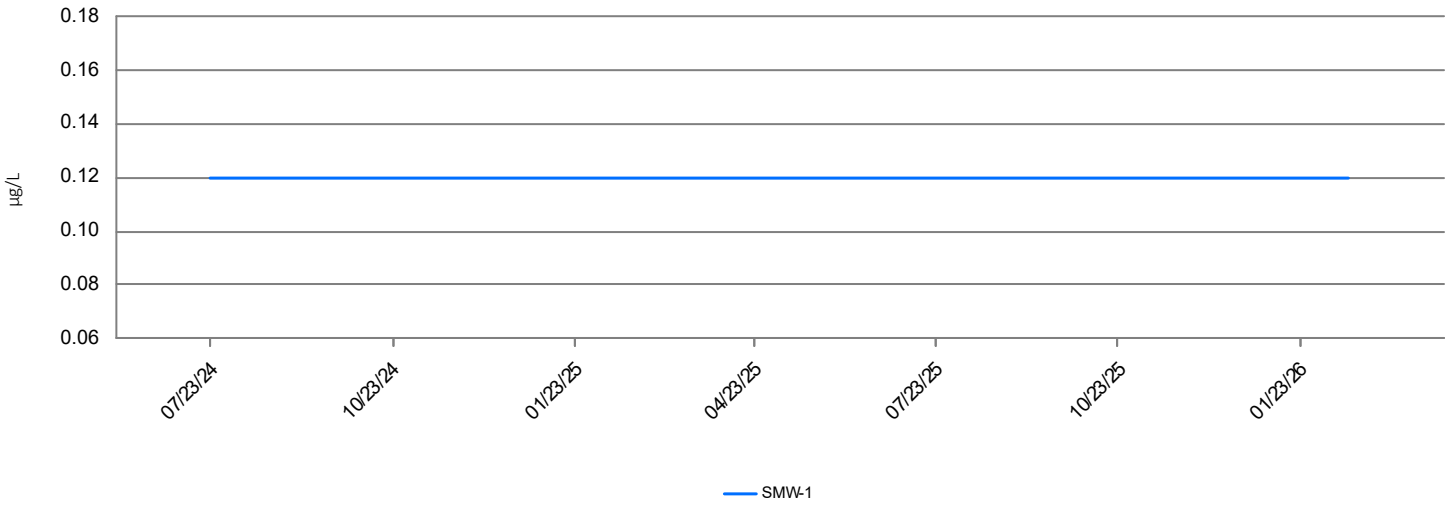
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

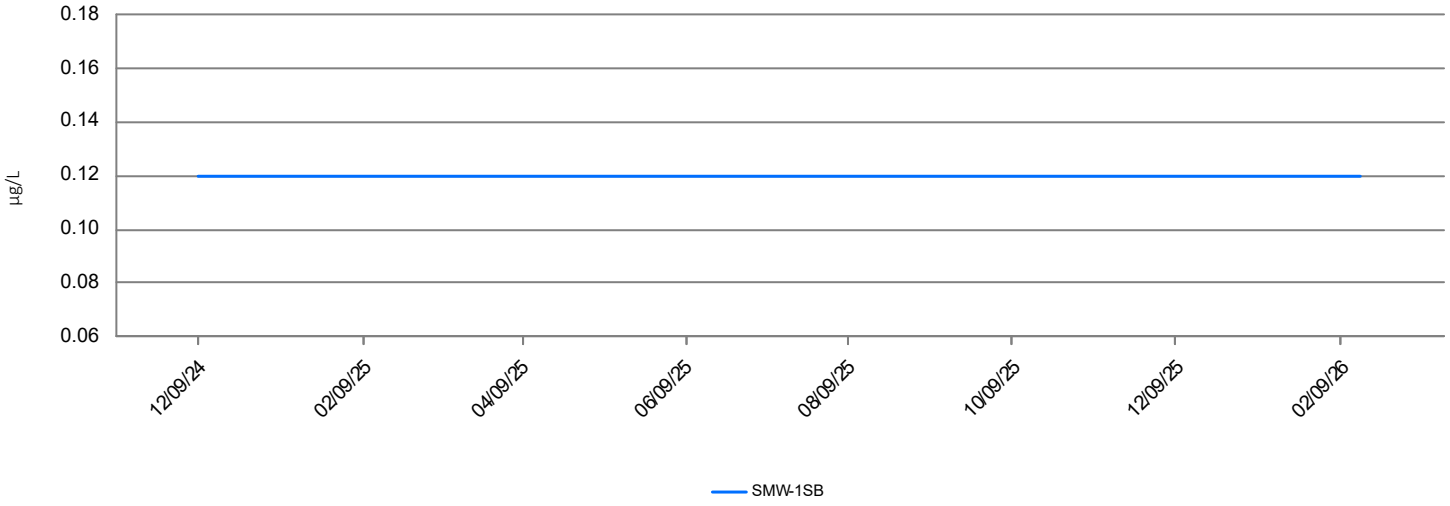
MonitorPro

No Group Selected, Silver, Dissolved (µg/L)

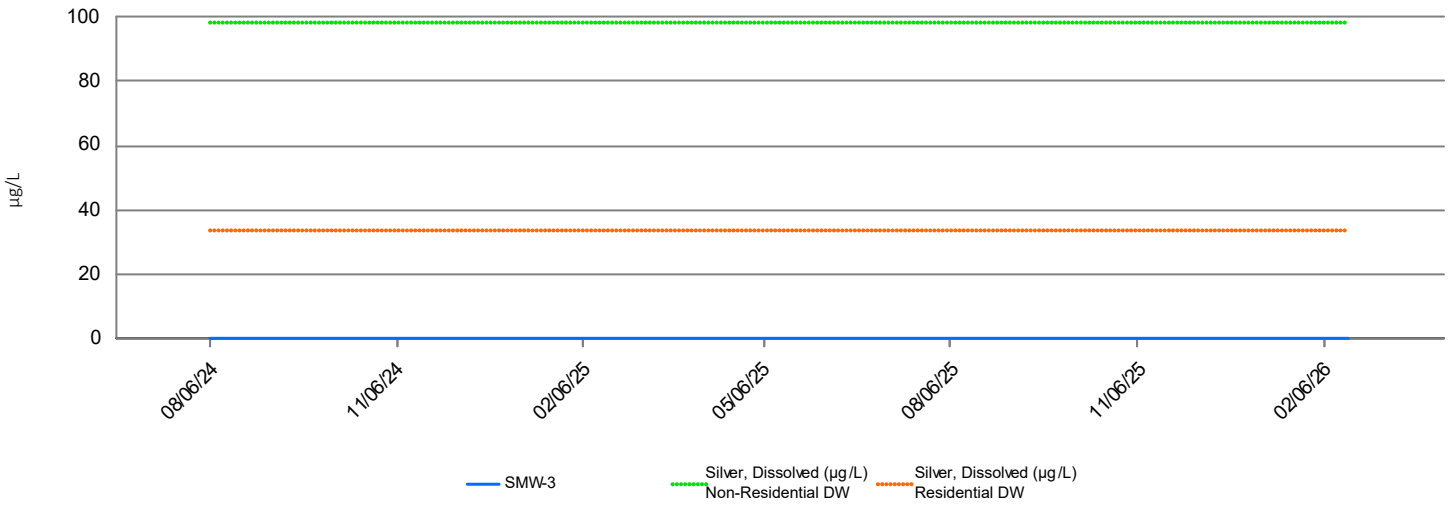
SMW-1



SMW-1SB



SMW-3

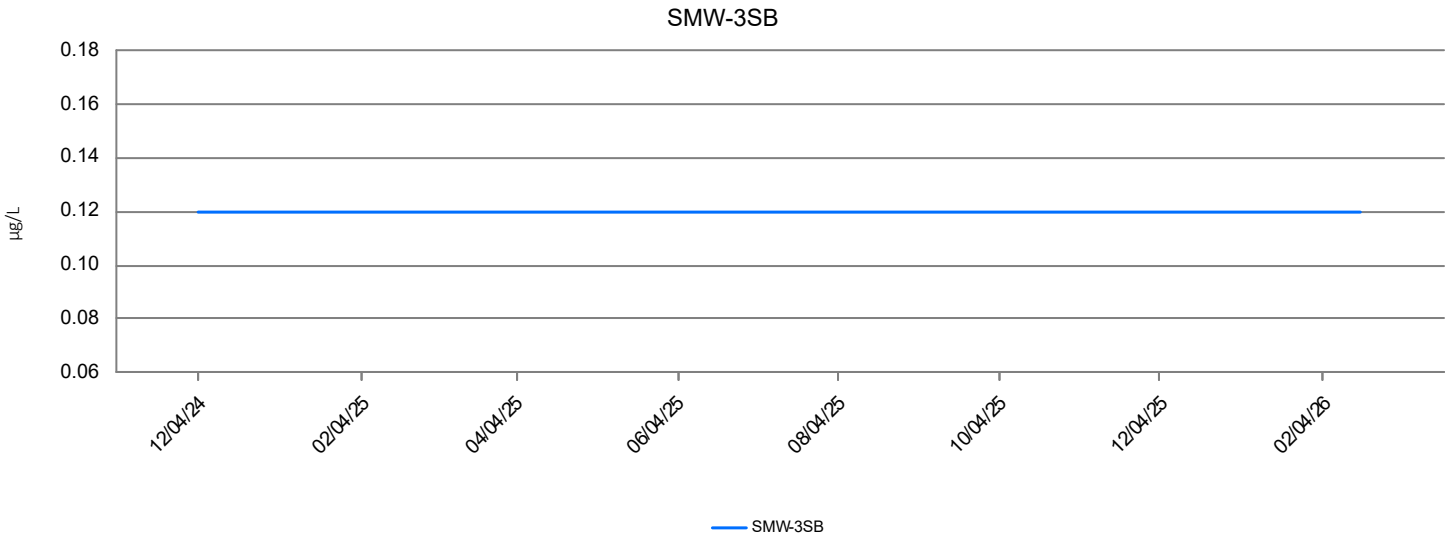


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Silver, Dissolved (µg/L)

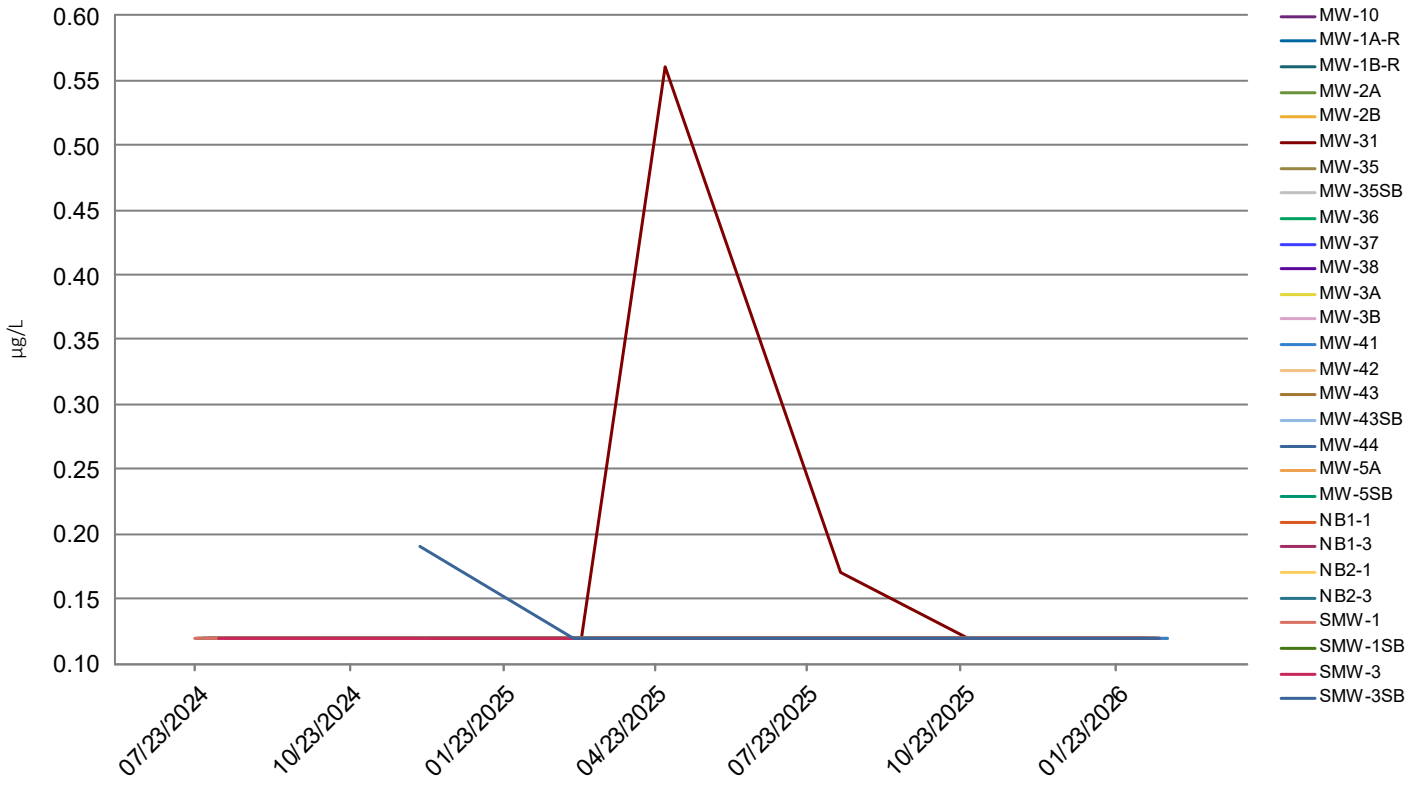


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Silver, Total Recoverable (µg/L)

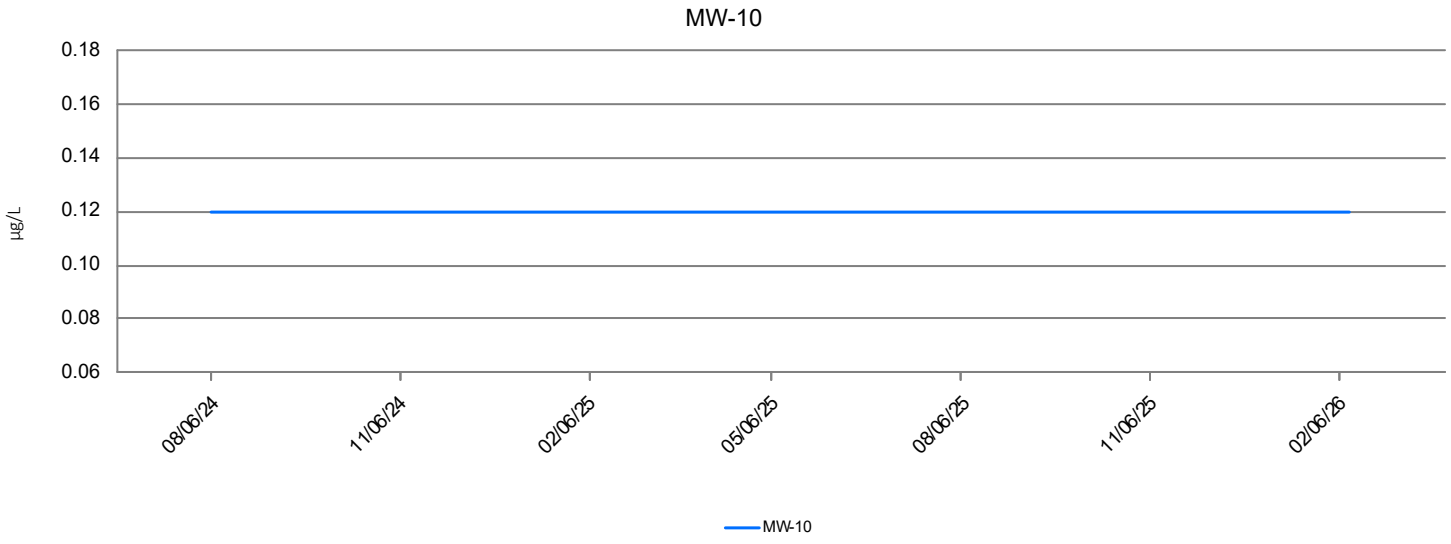


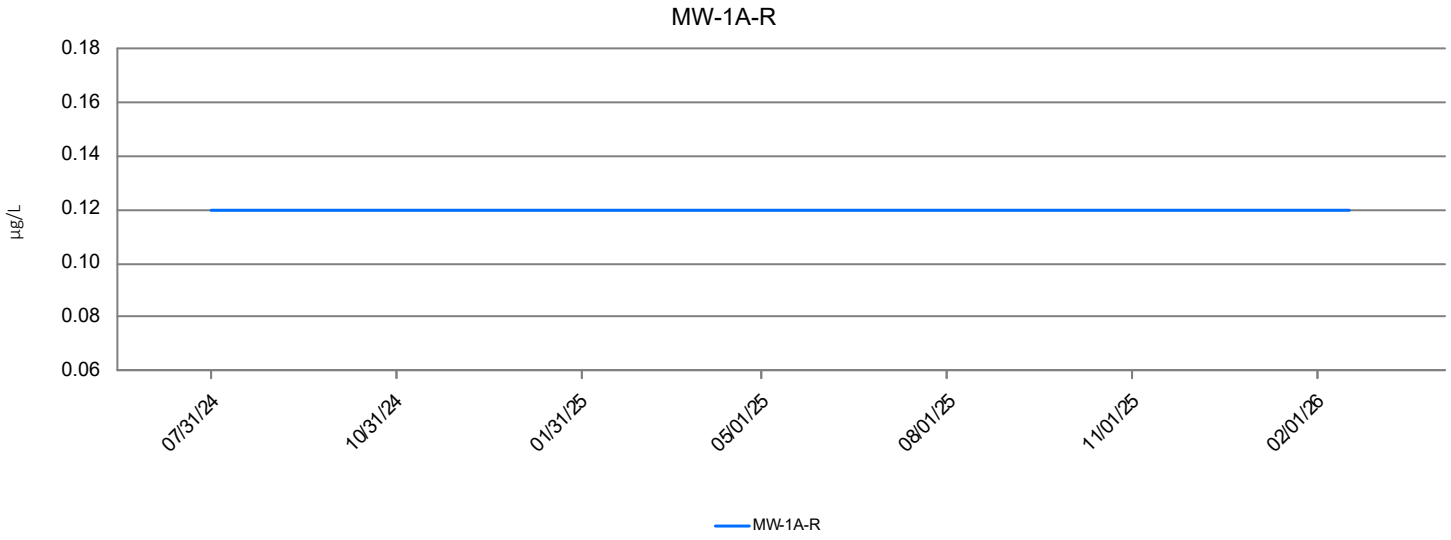
Variable Graphical Report

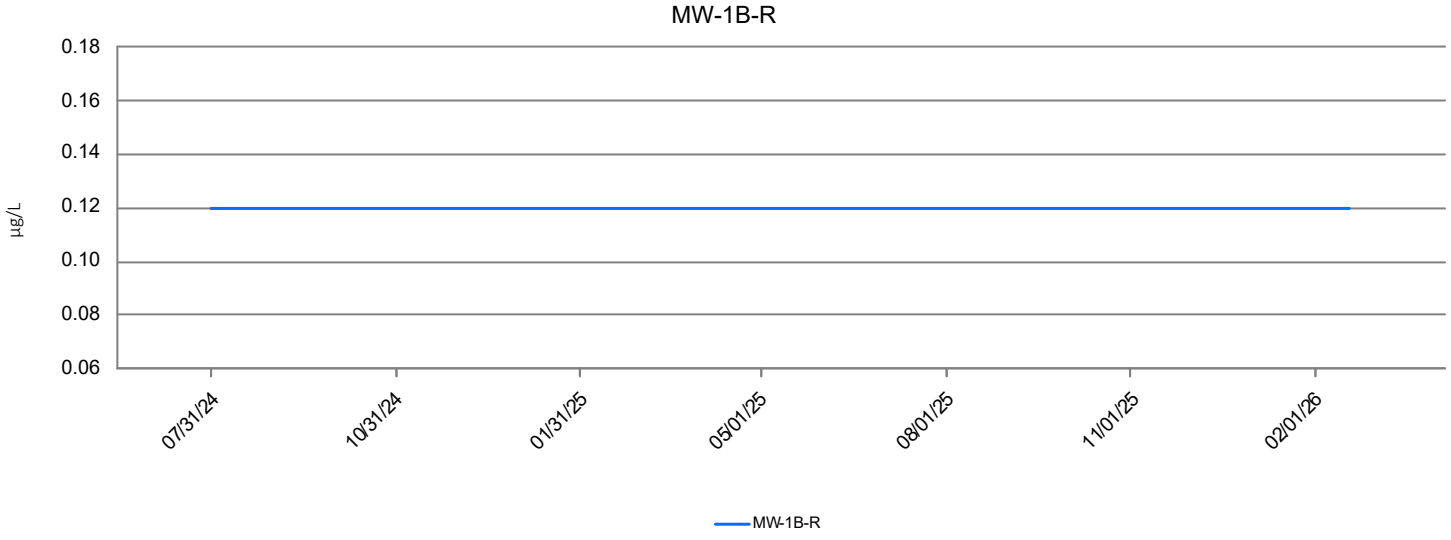
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Silver, Total Recoverable (µg/L)







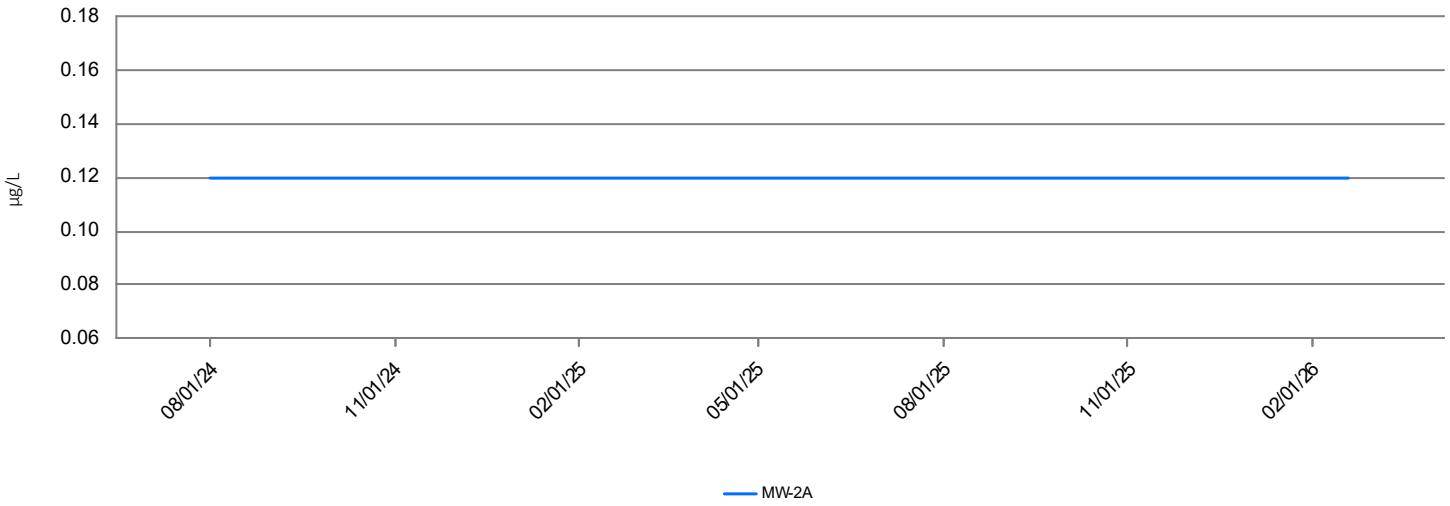
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

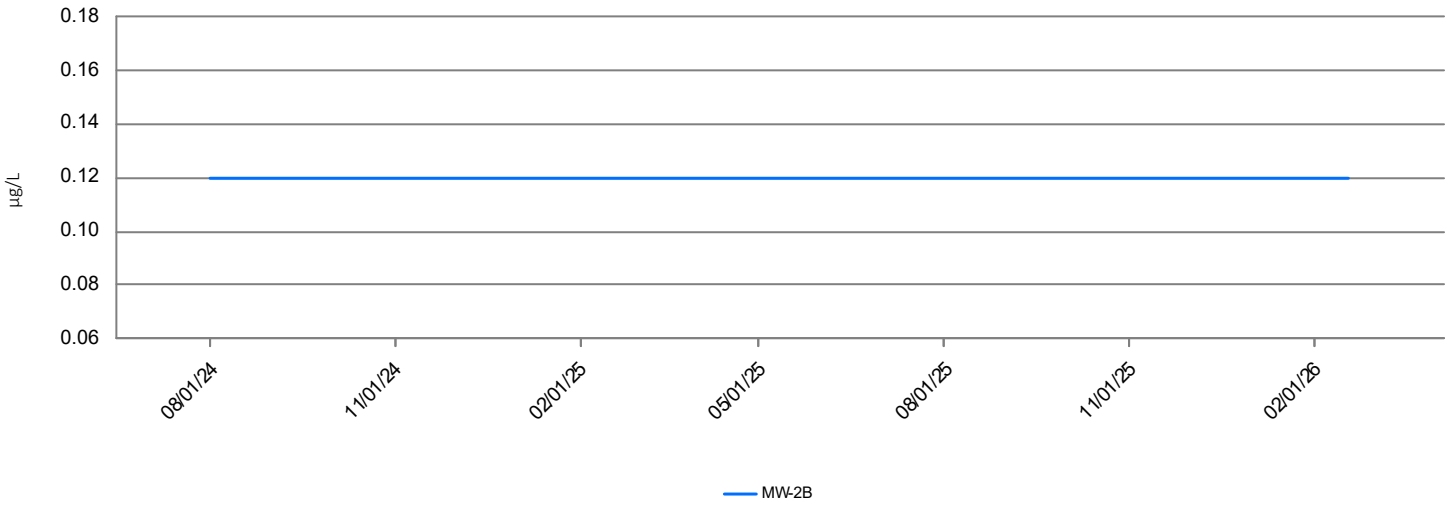
MonitorPro

No Group Selected, Silver, Total Recoverable (µg/L)

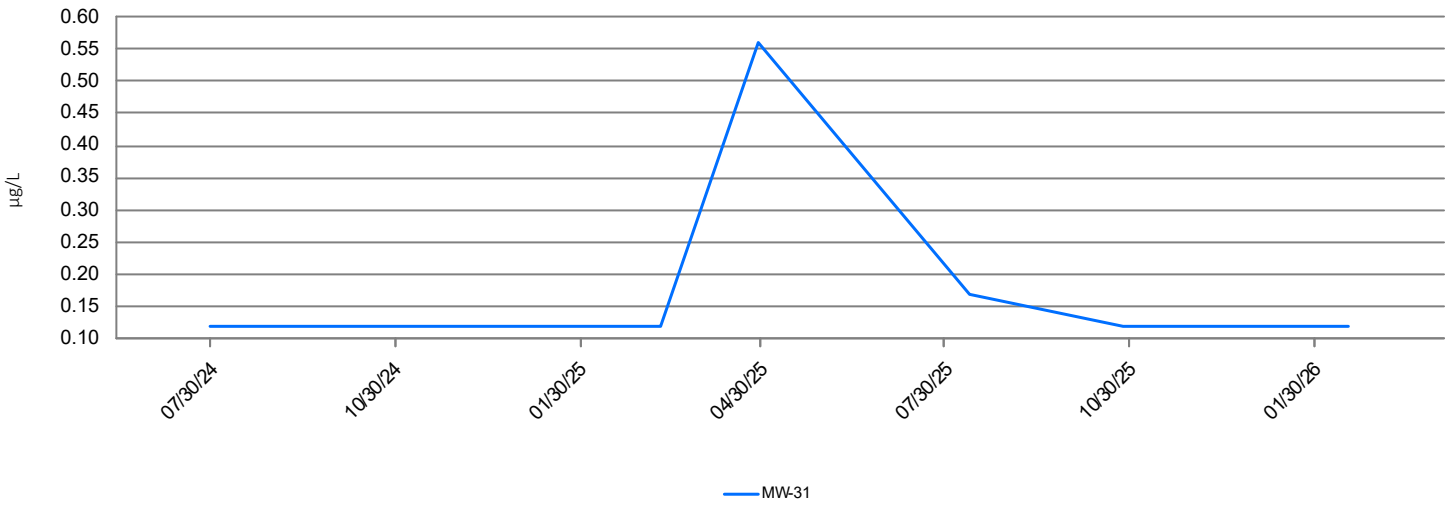
MW-2A



MW-2B



MW-31

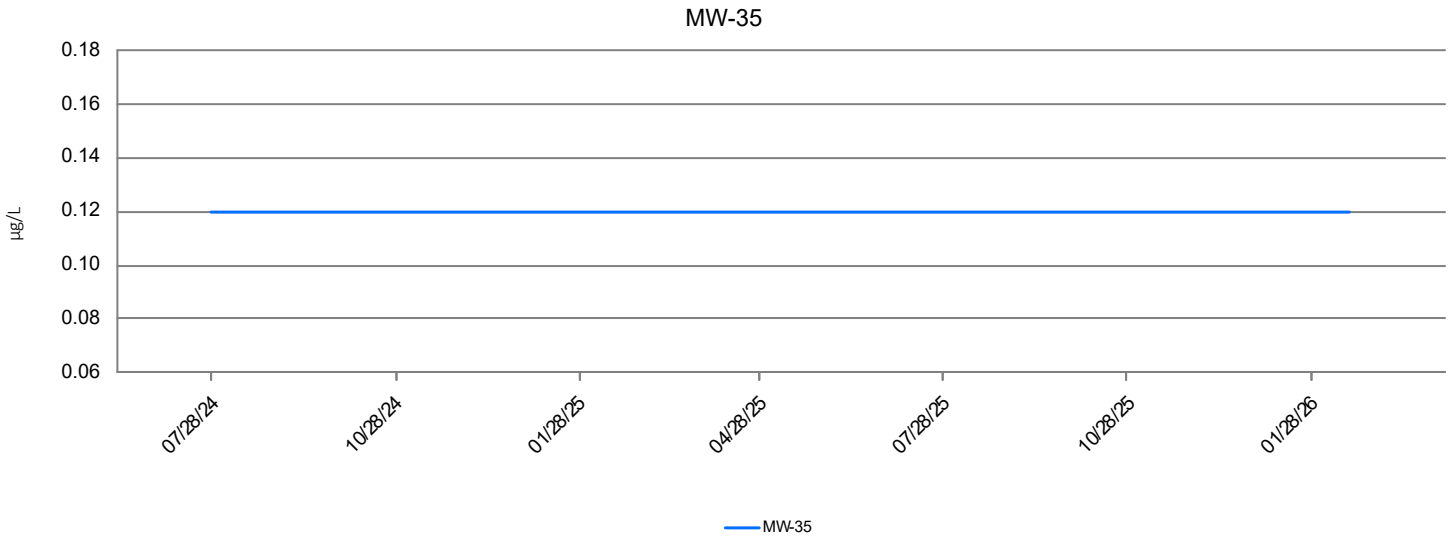


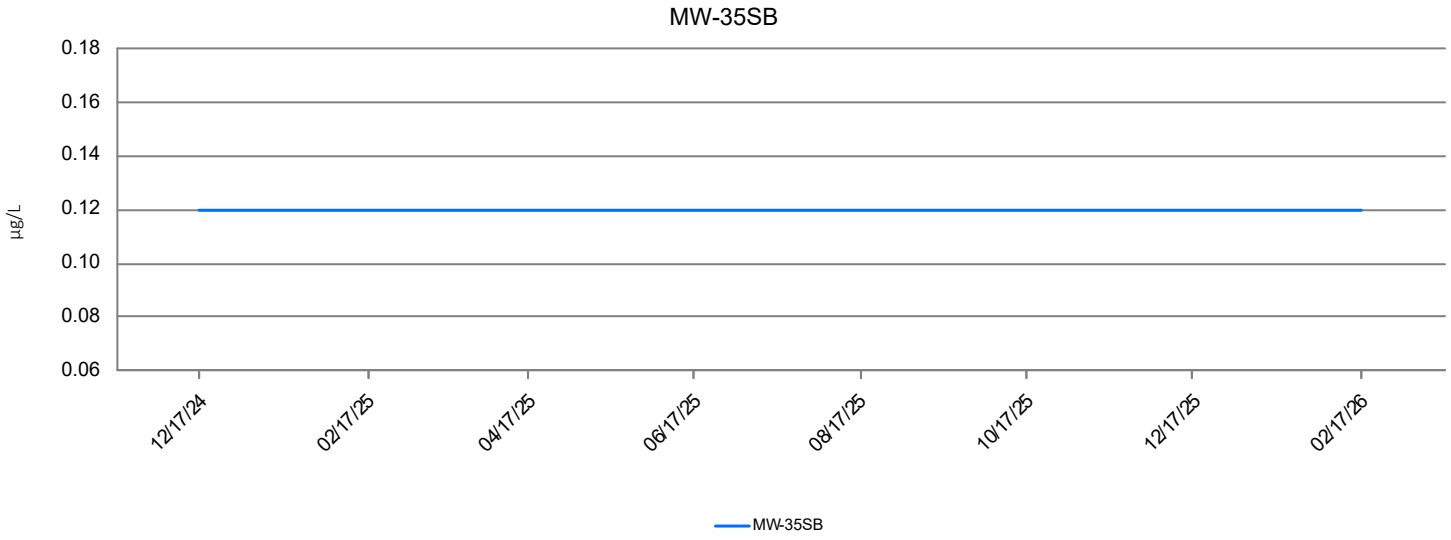
Variable Graphical Report

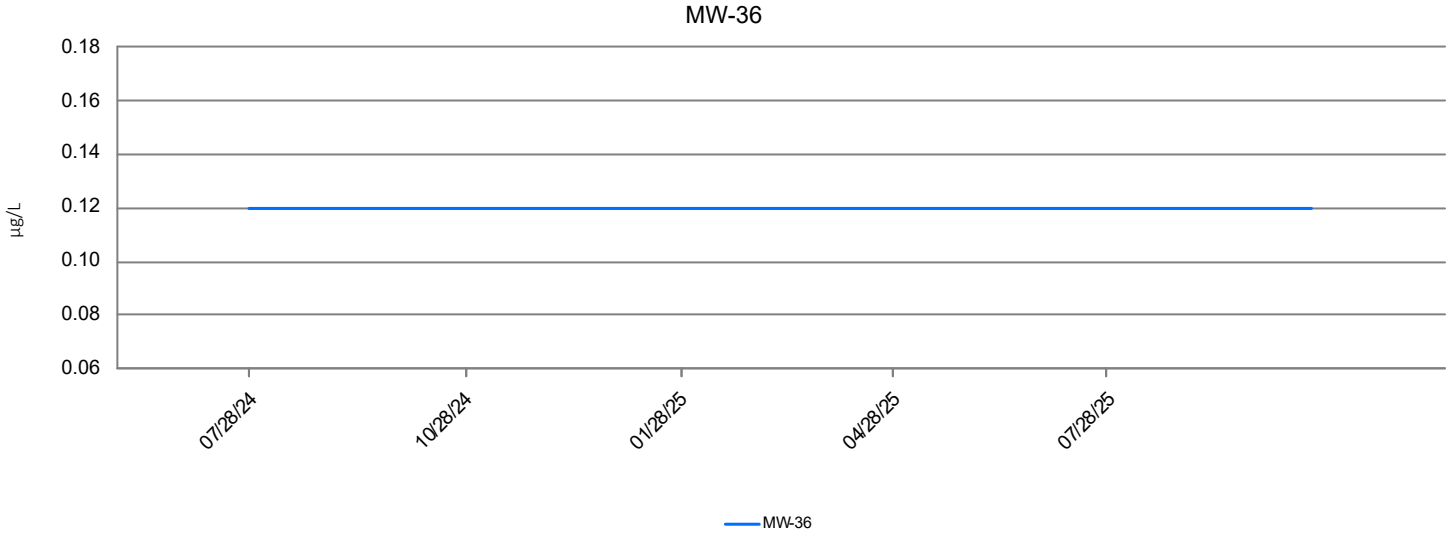
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Silver, Total Recoverable (µg/L)





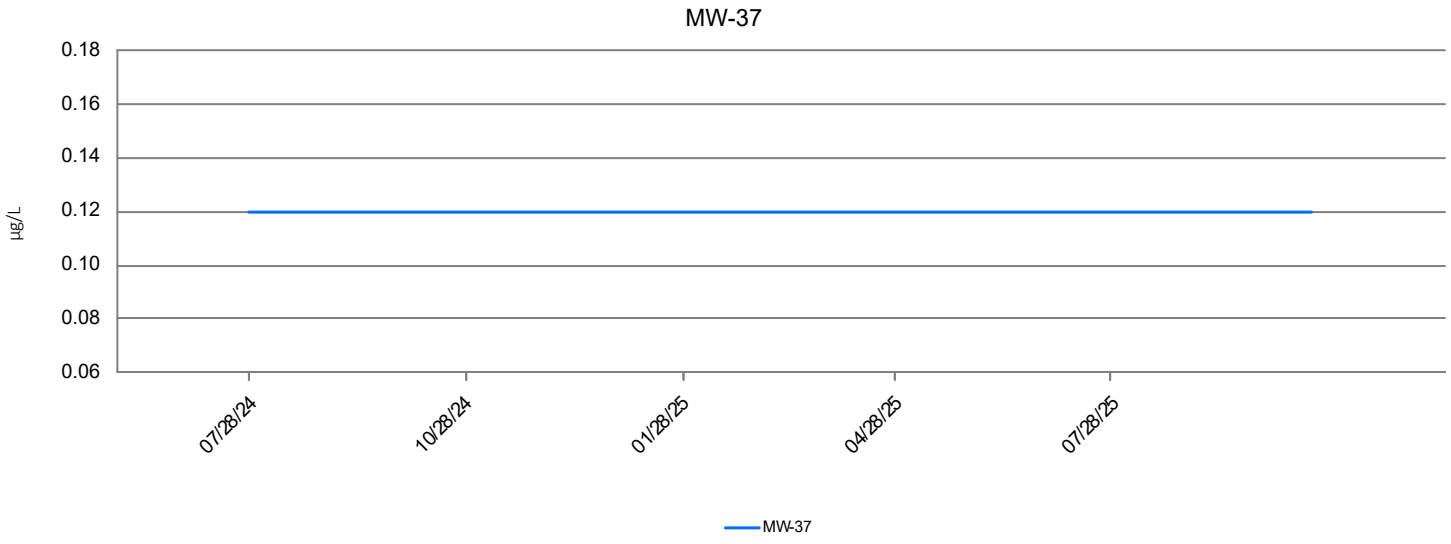


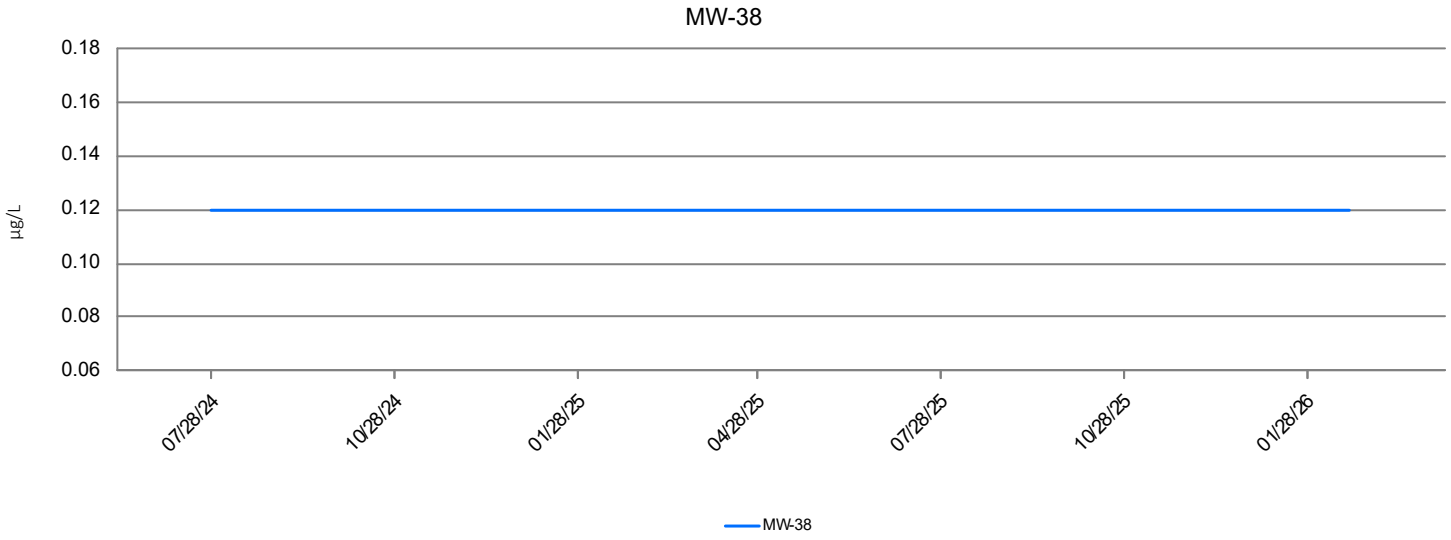
Variable Graphical Report

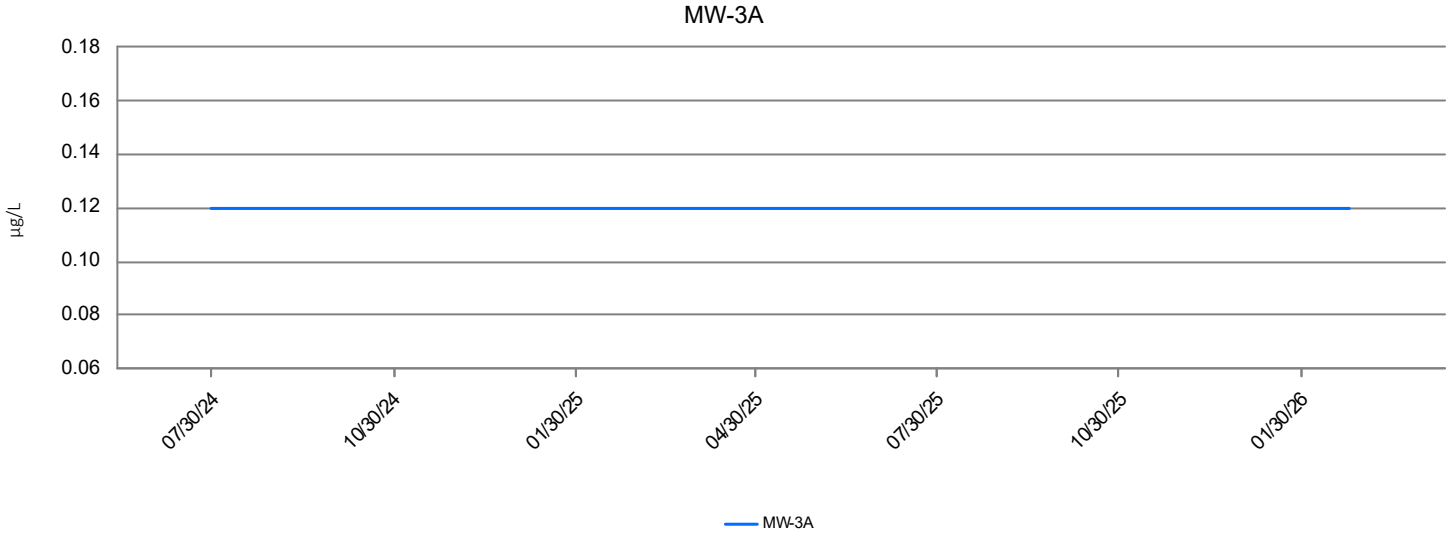
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Silver, Total Recoverable (µg/L)





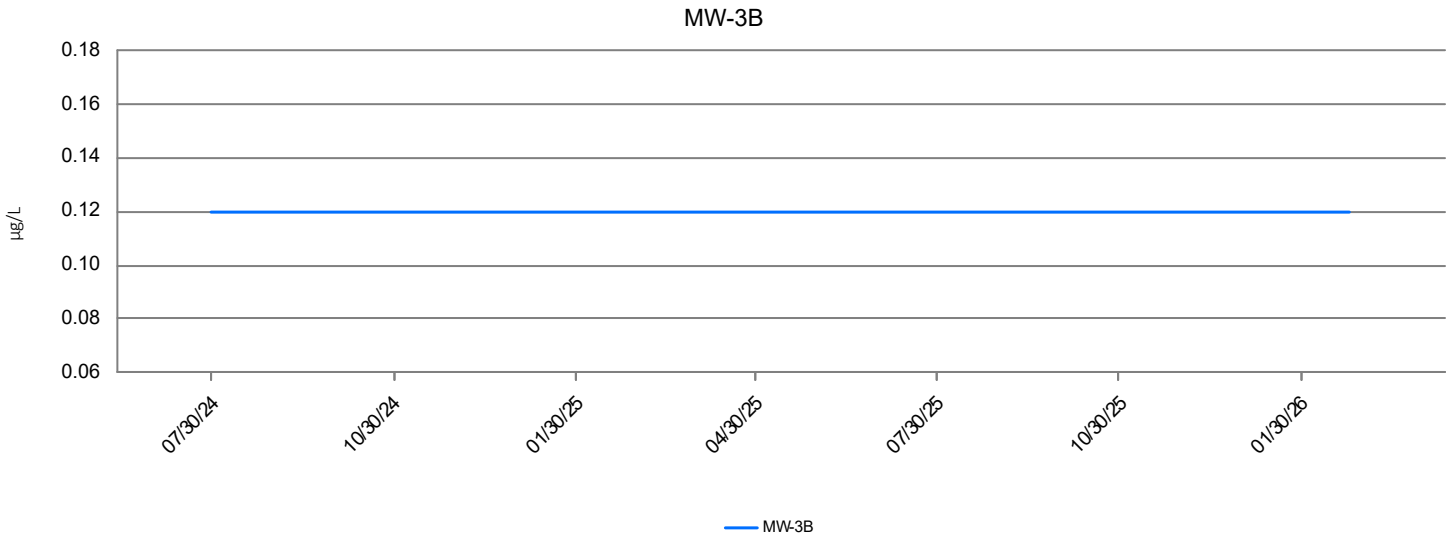


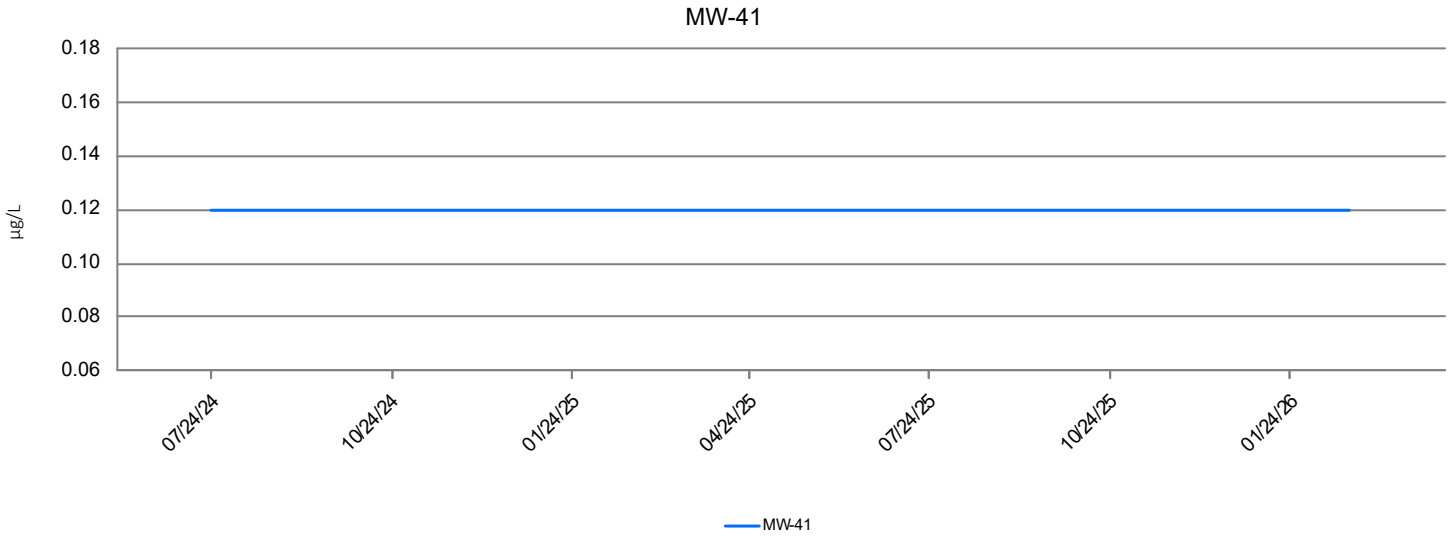
Variable Graphical Report

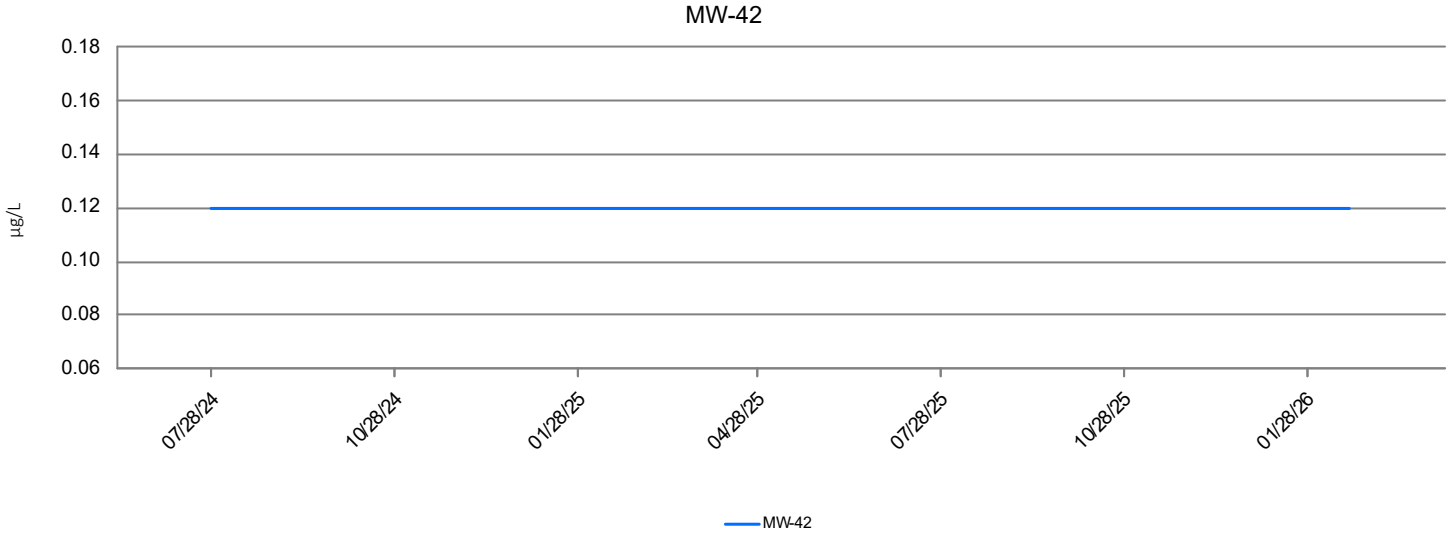
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Silver, Total Recoverable (µg/L)







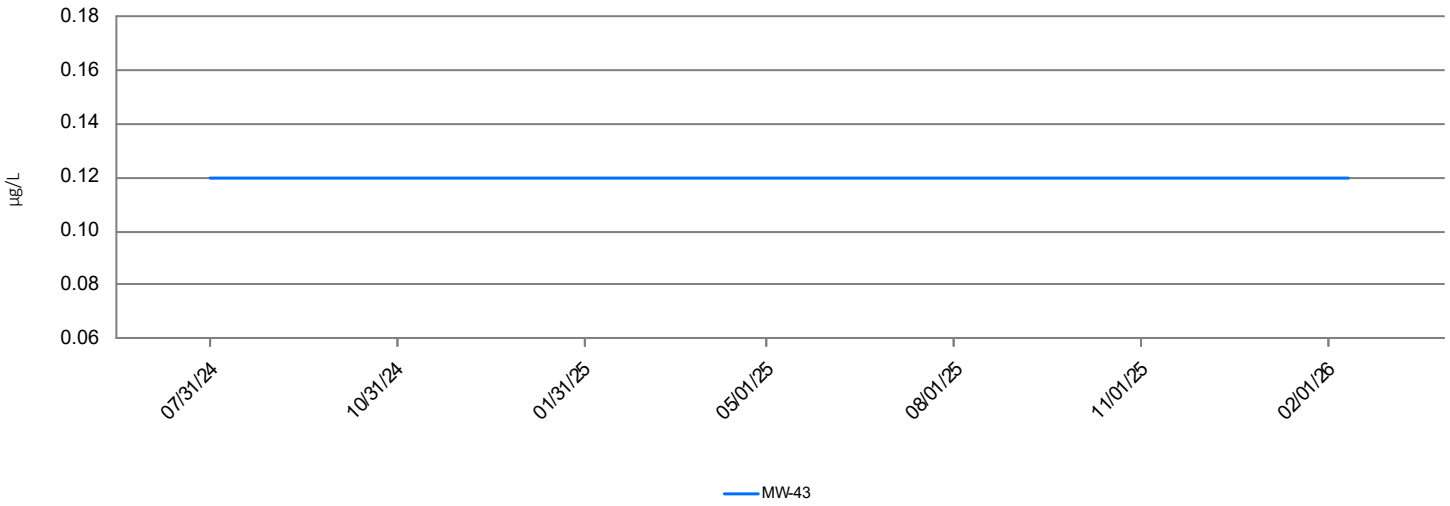
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

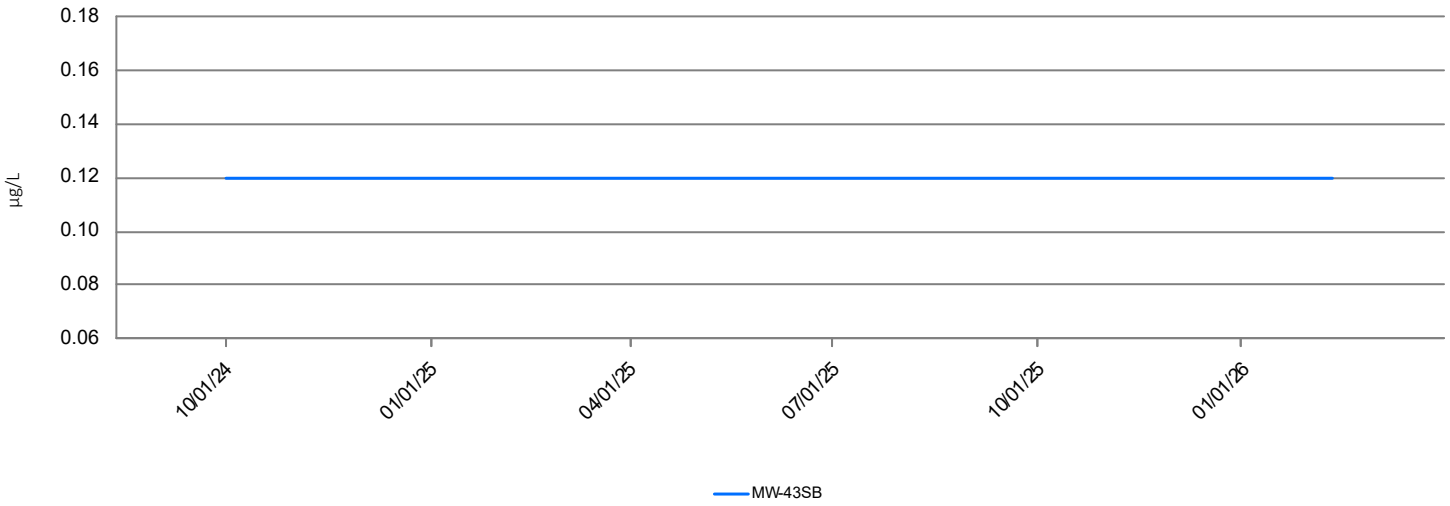
MonitorPro

No Group Selected, Silver, Total Recoverable (µg/L)

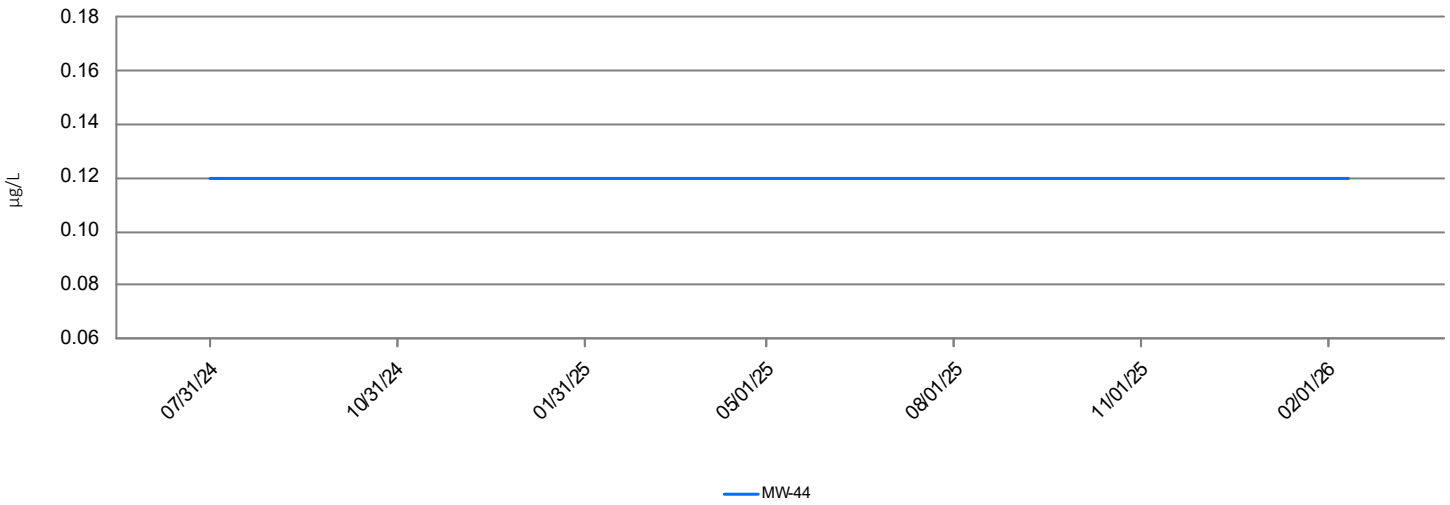
MW-43



MW-43SB



MW-44

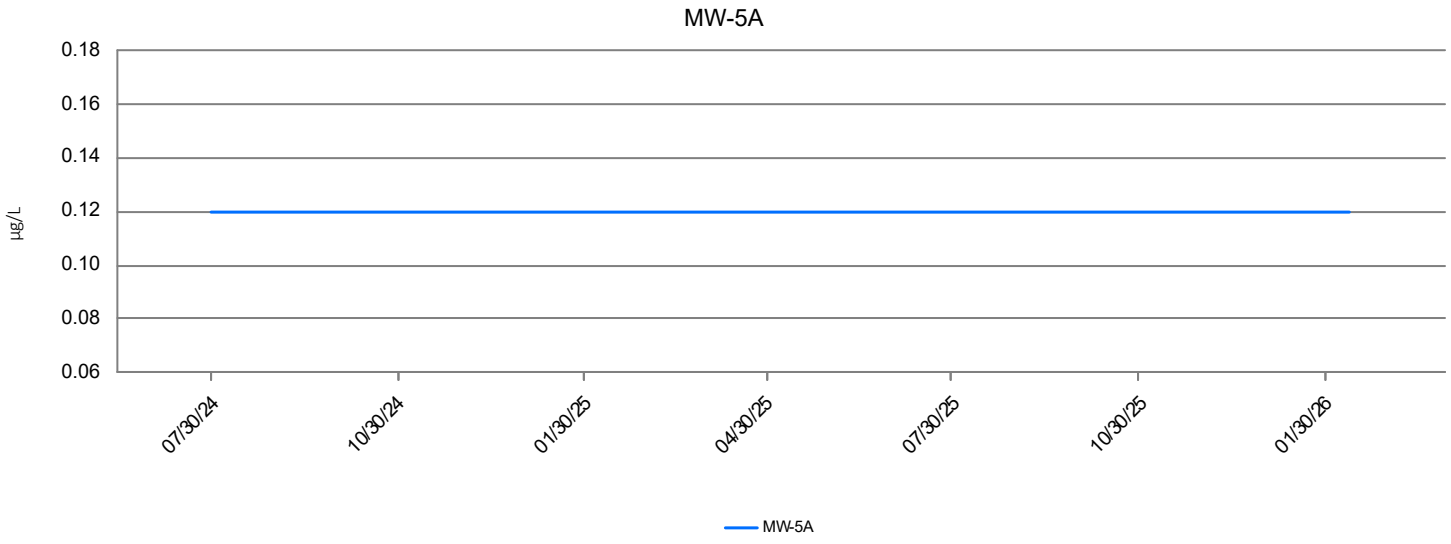


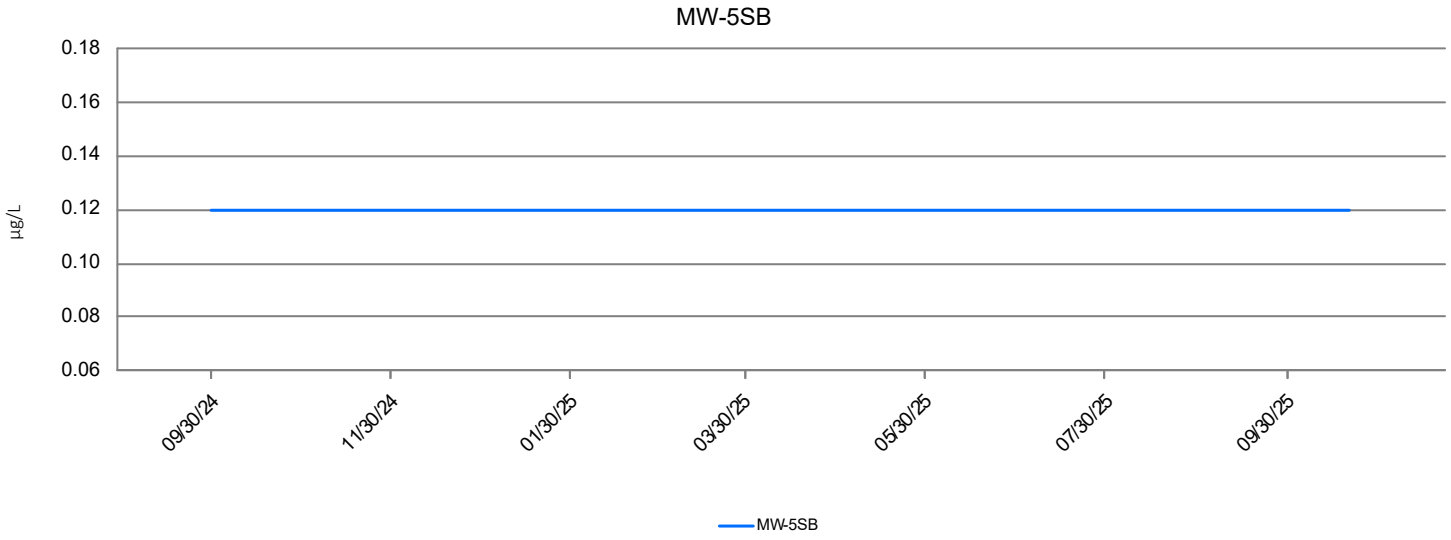
Variable Graphical Report

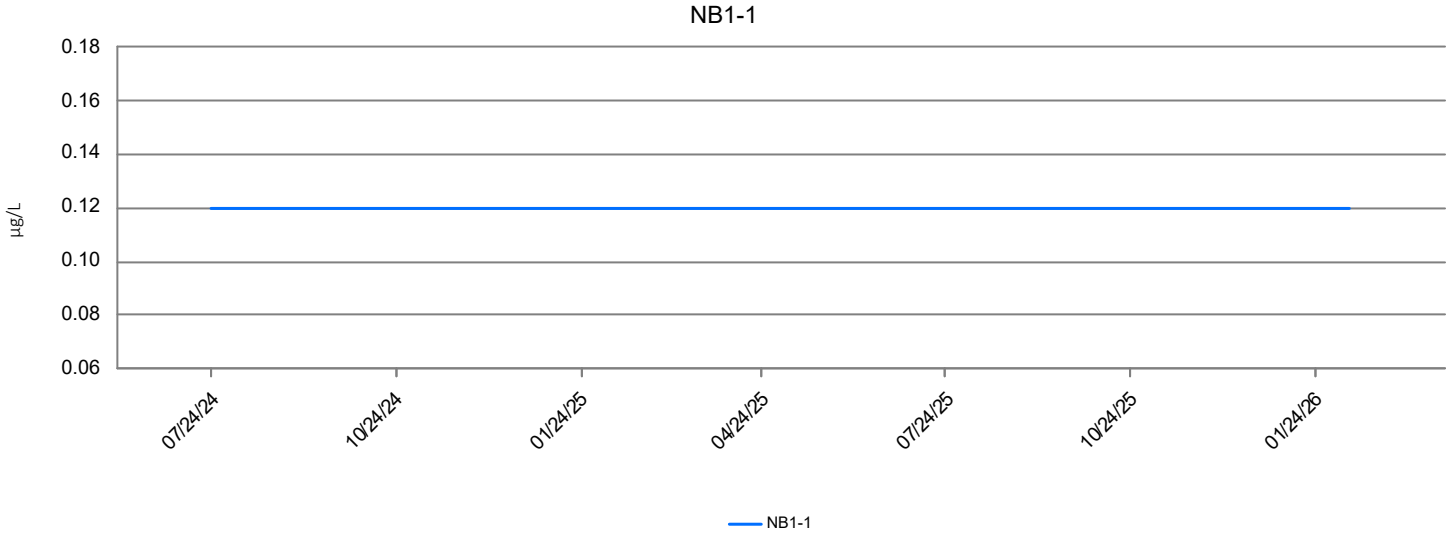
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Silver, Total Recoverable (µg/L)





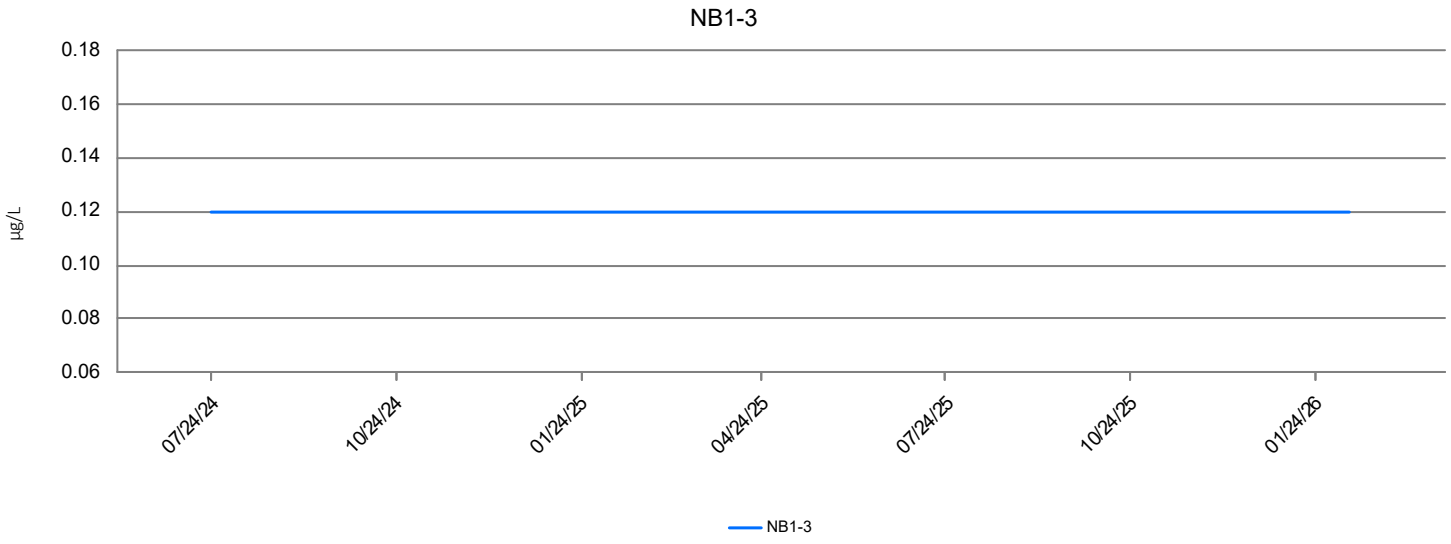


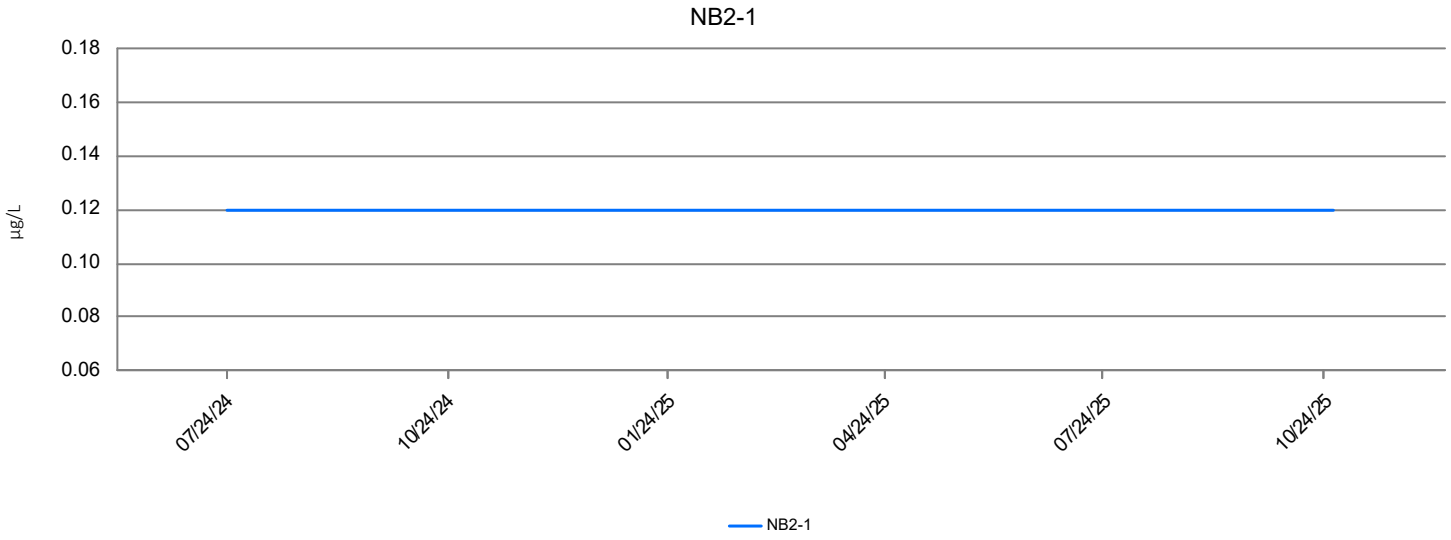
Variable Graphical Report

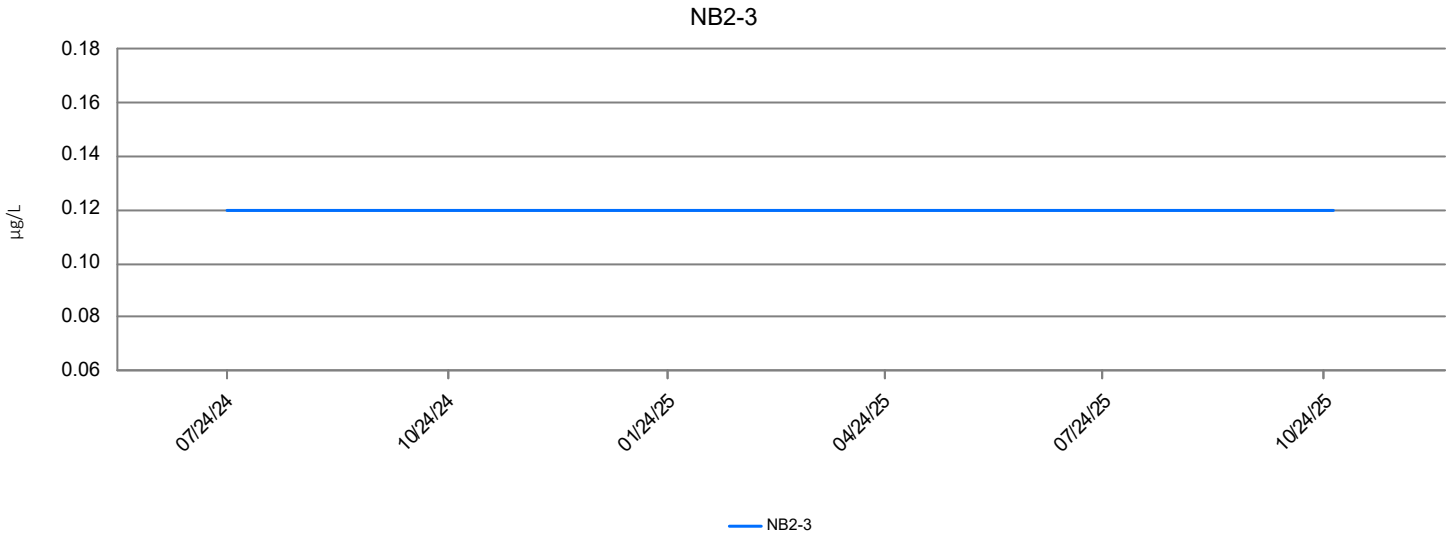
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Silver, Total Recoverable (µg/L)







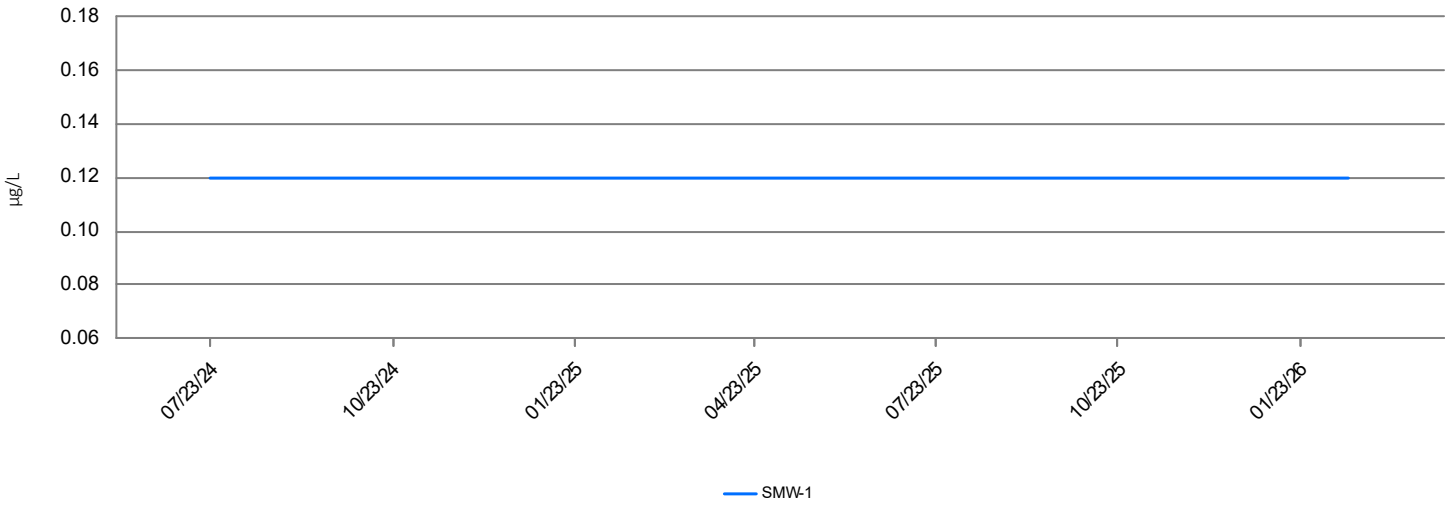
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

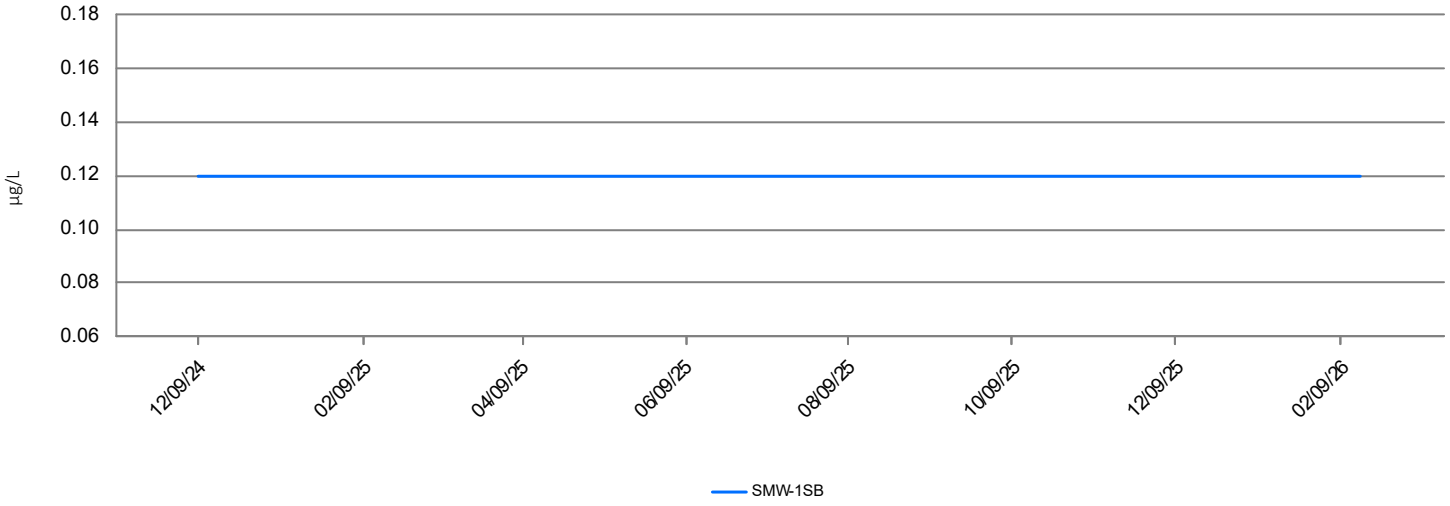
MonitorPro

No Group Selected, Silver, Total Recoverable (µg/L)

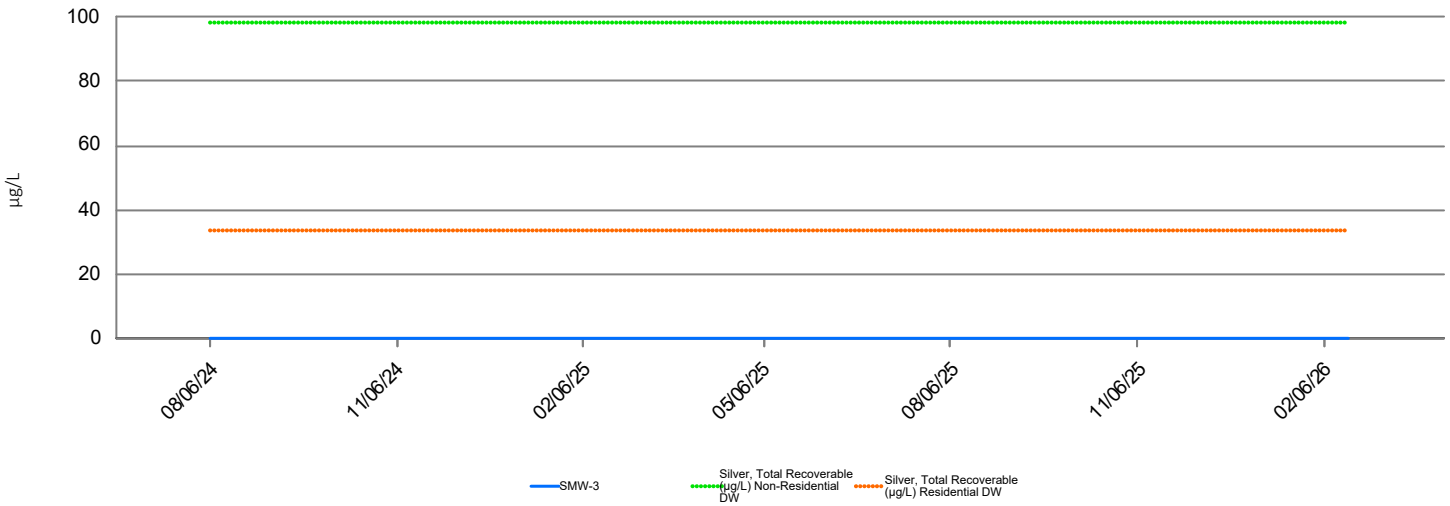
SMW-1



SMW-1SB



SMW-3



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EHS DATA

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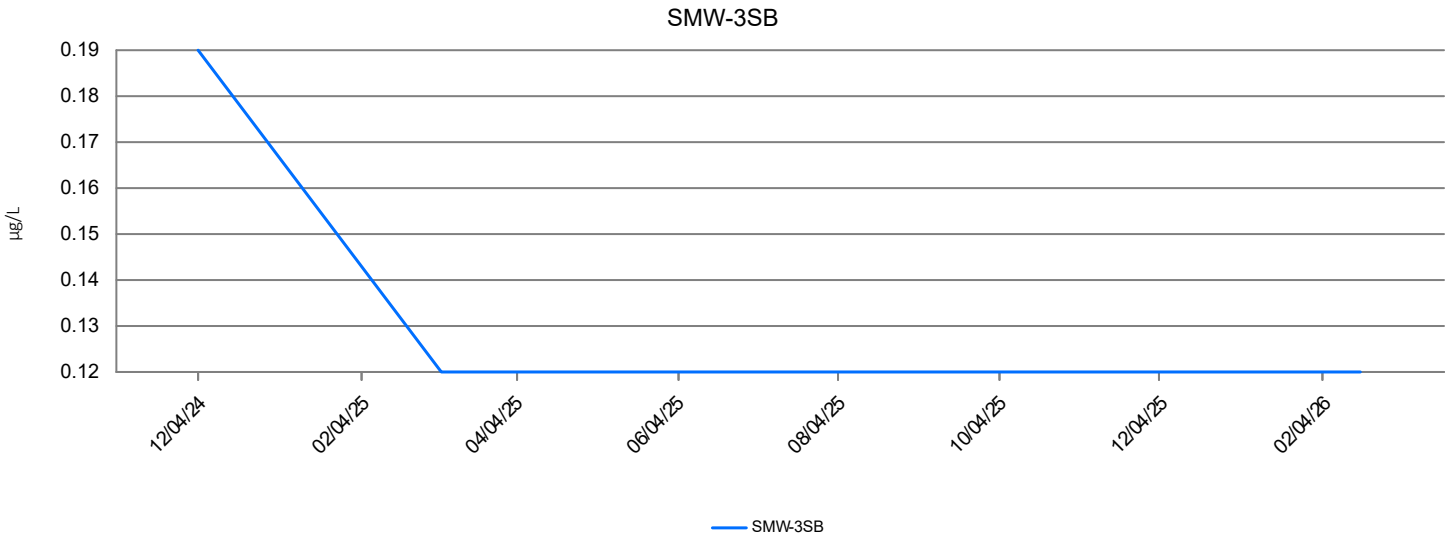
MCERTS

Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Silver, Total Recoverable (µg/L)

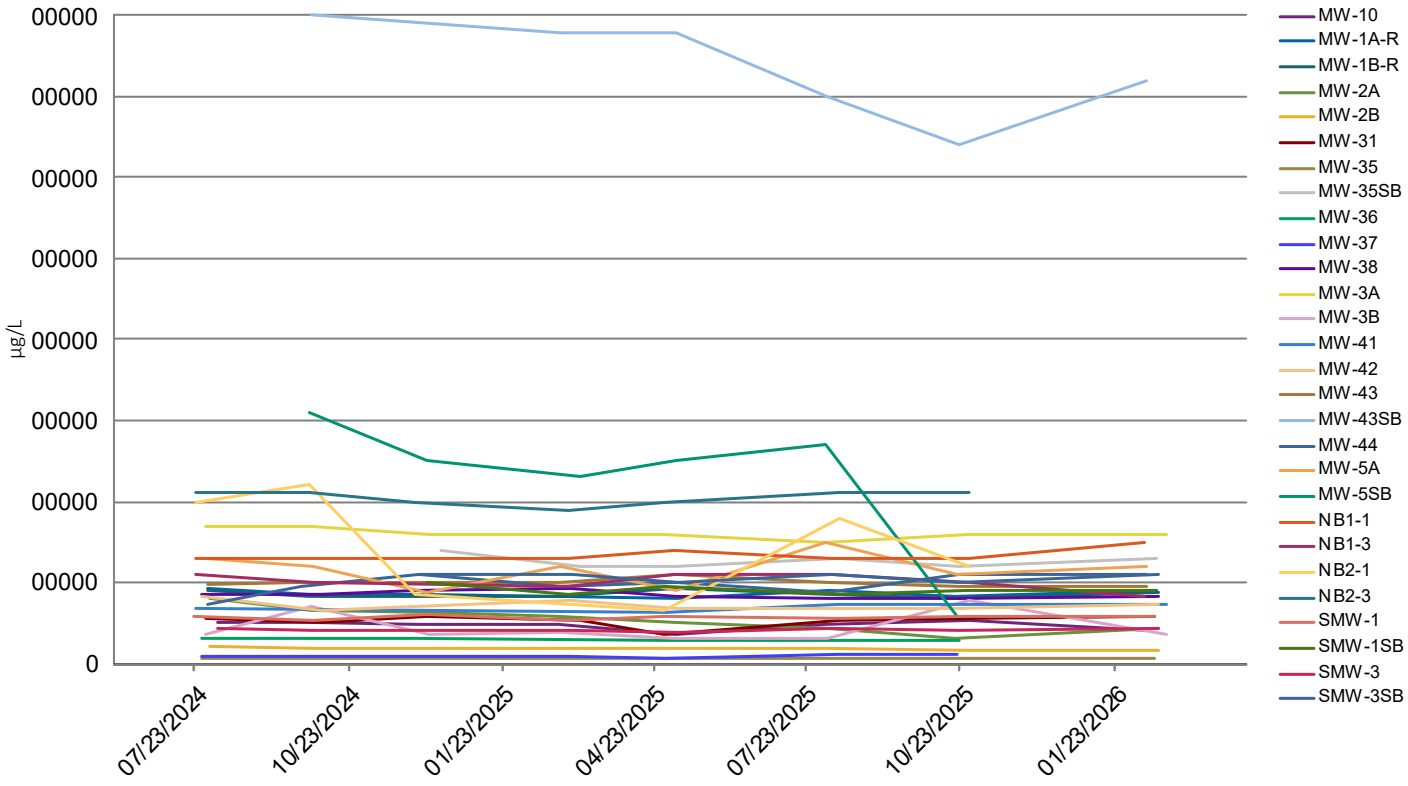


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sodium, Dissolved (µg/L)

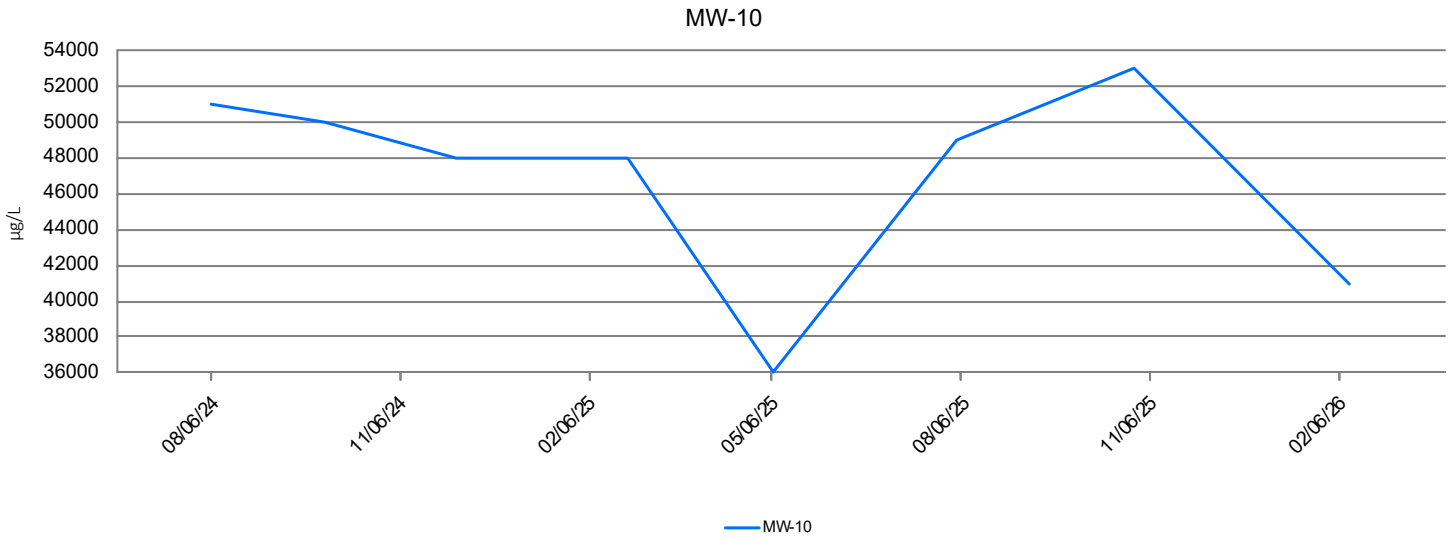


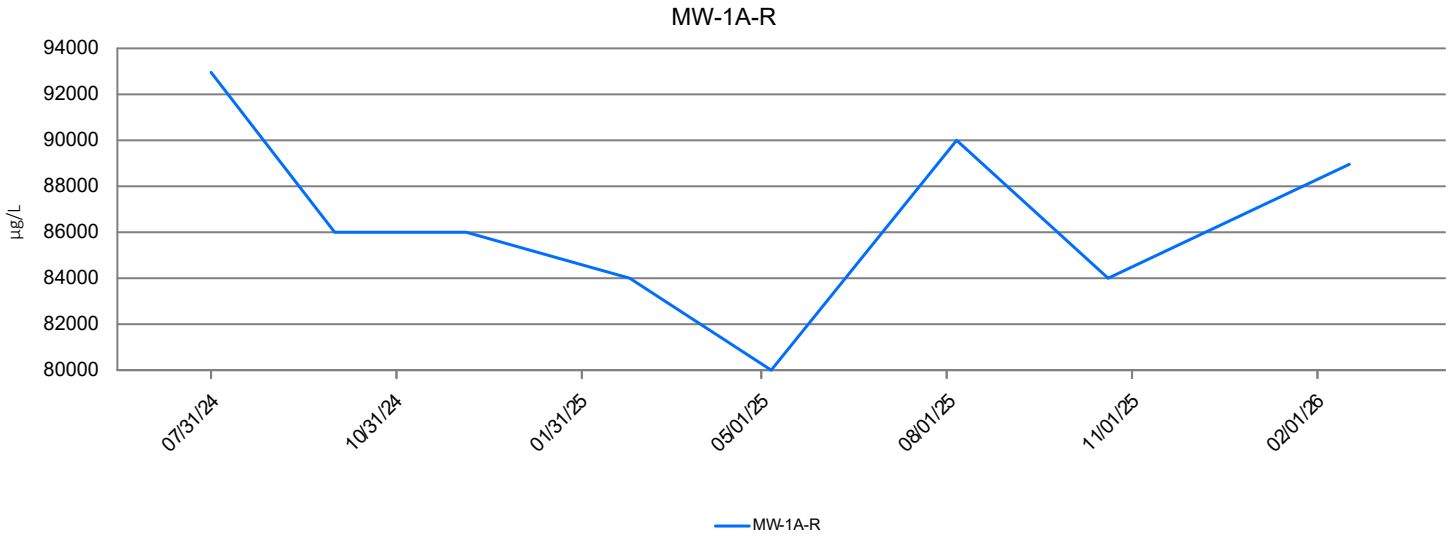
Variable Graphical Report

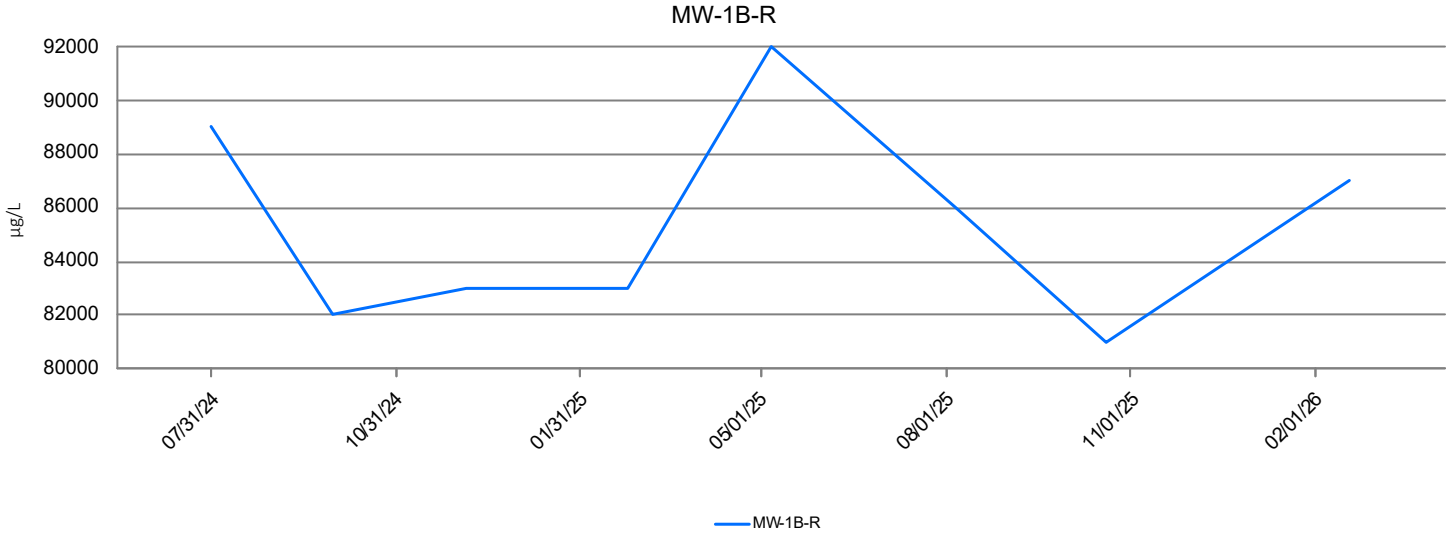
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sodium, Dissolved (µg/L)







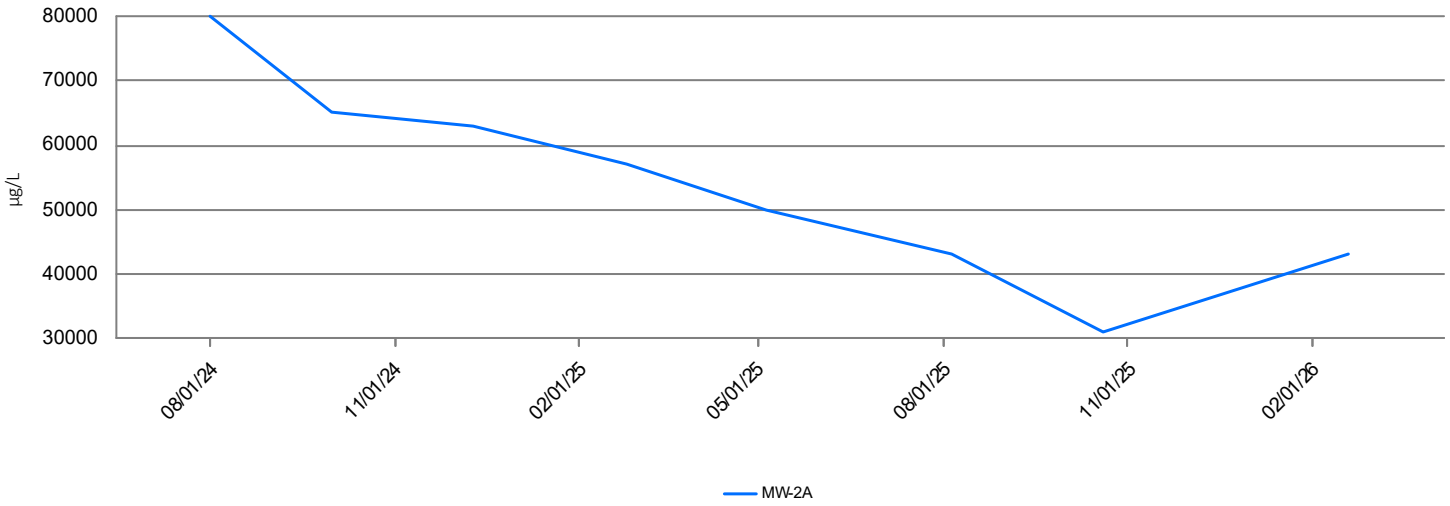
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

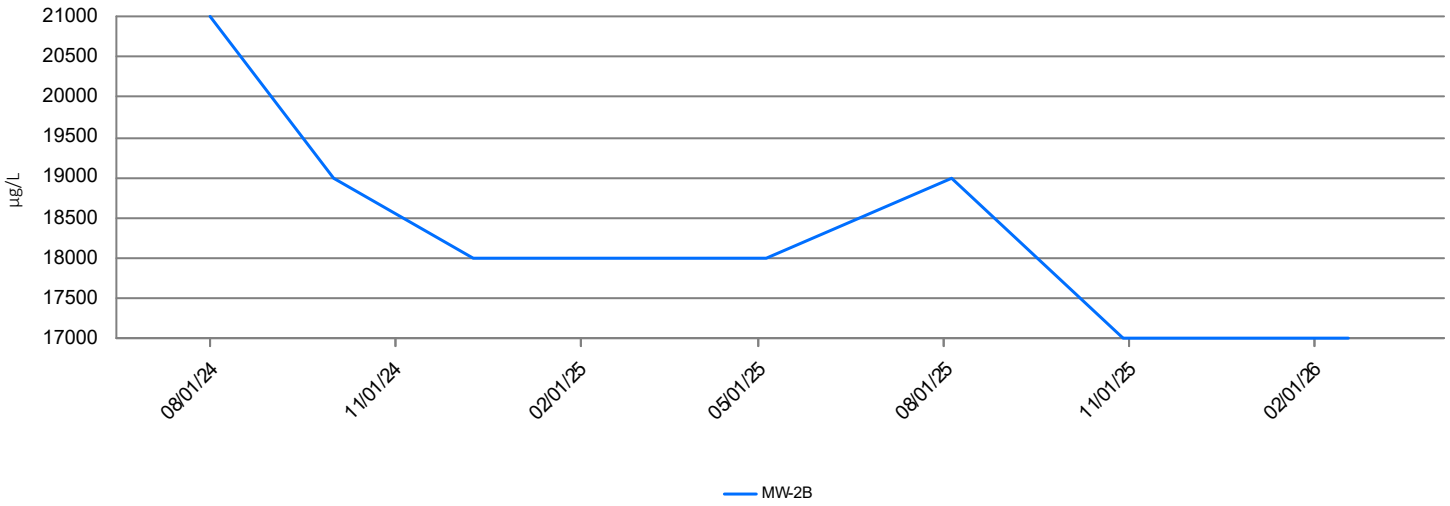
MonitorPro

No Group Selected, Sodium, Dissolved (µg/L)

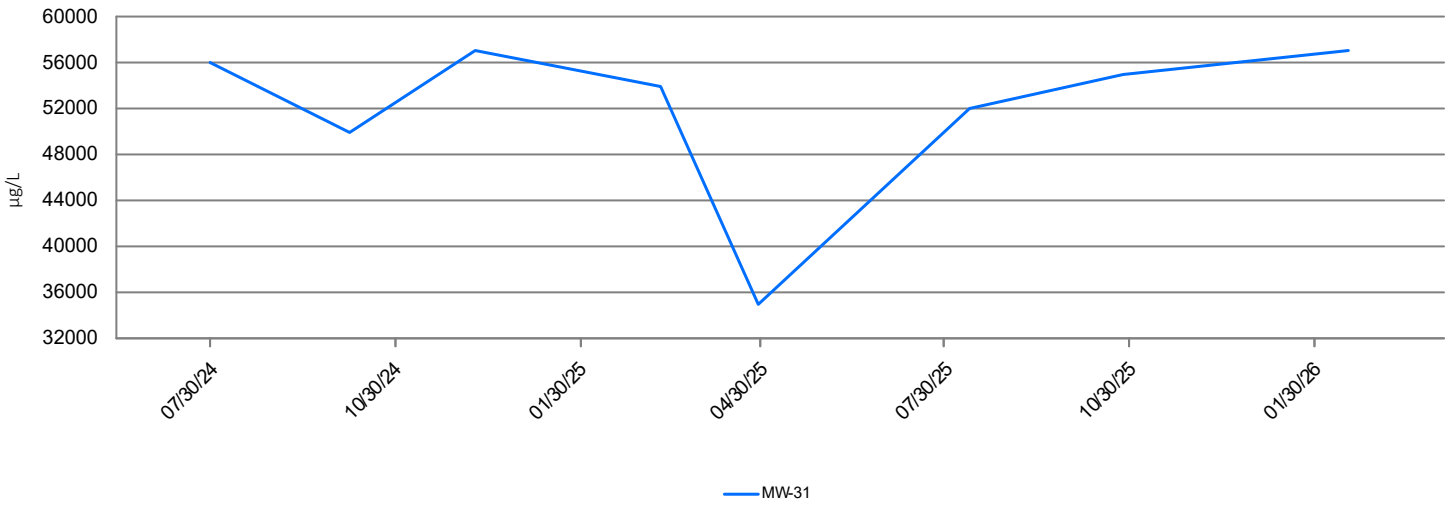
MW-2A



MW-2B



MW-31

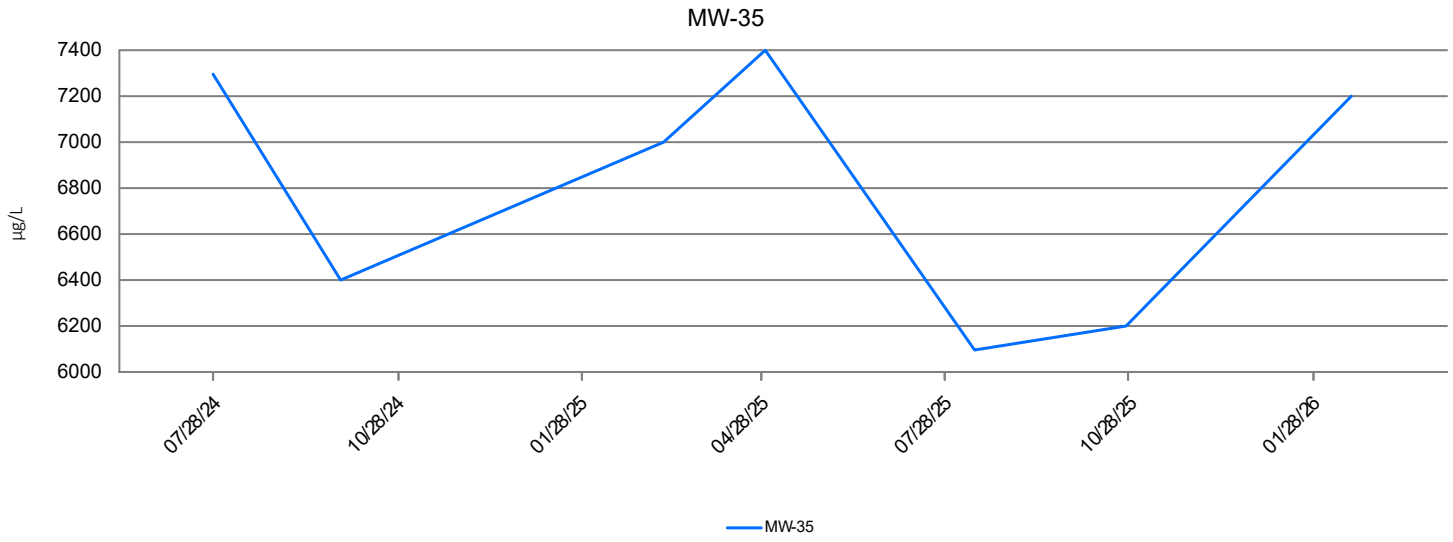


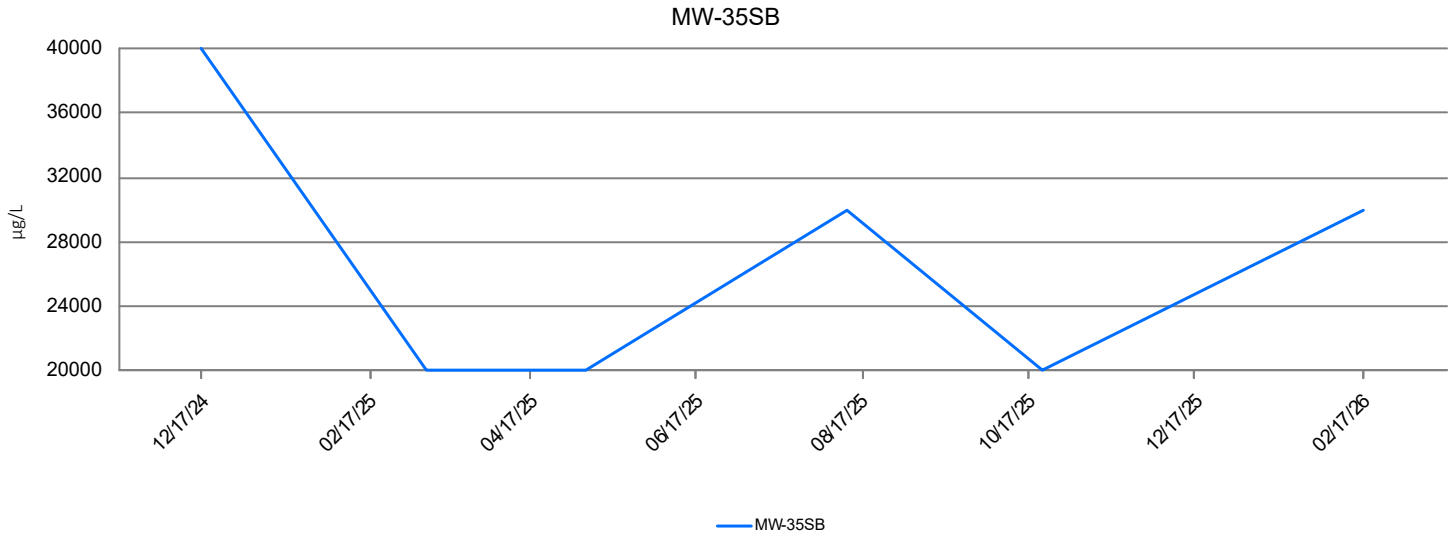
Variable Graphical Report

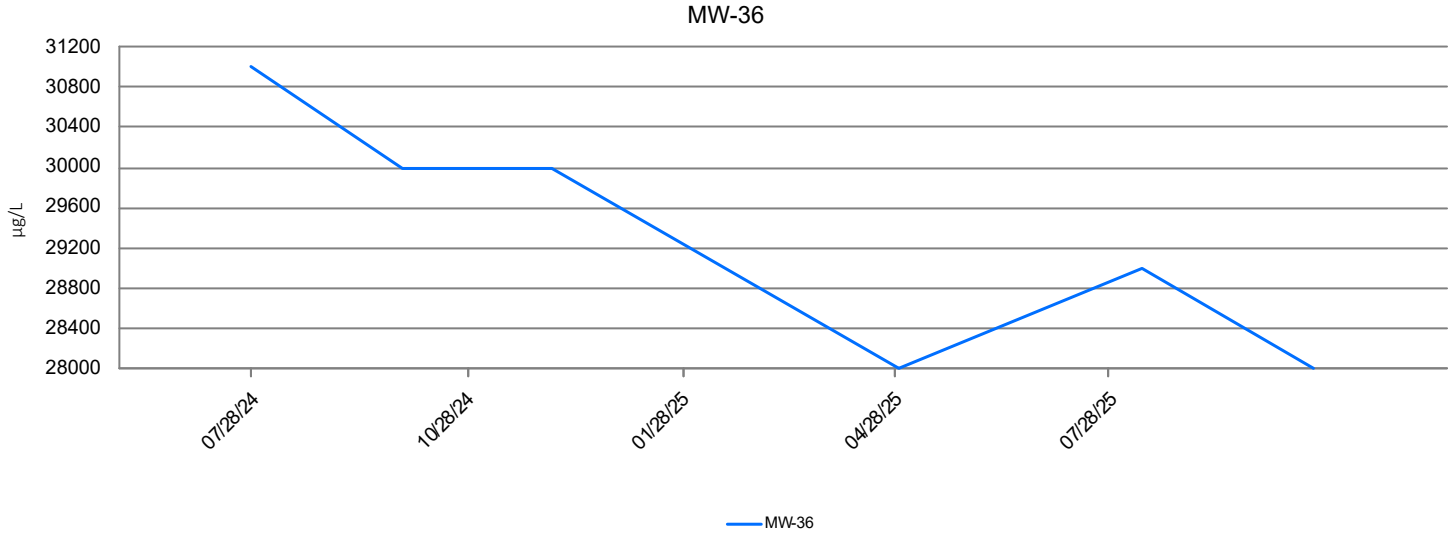
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sodium, Dissolved (µg/L)





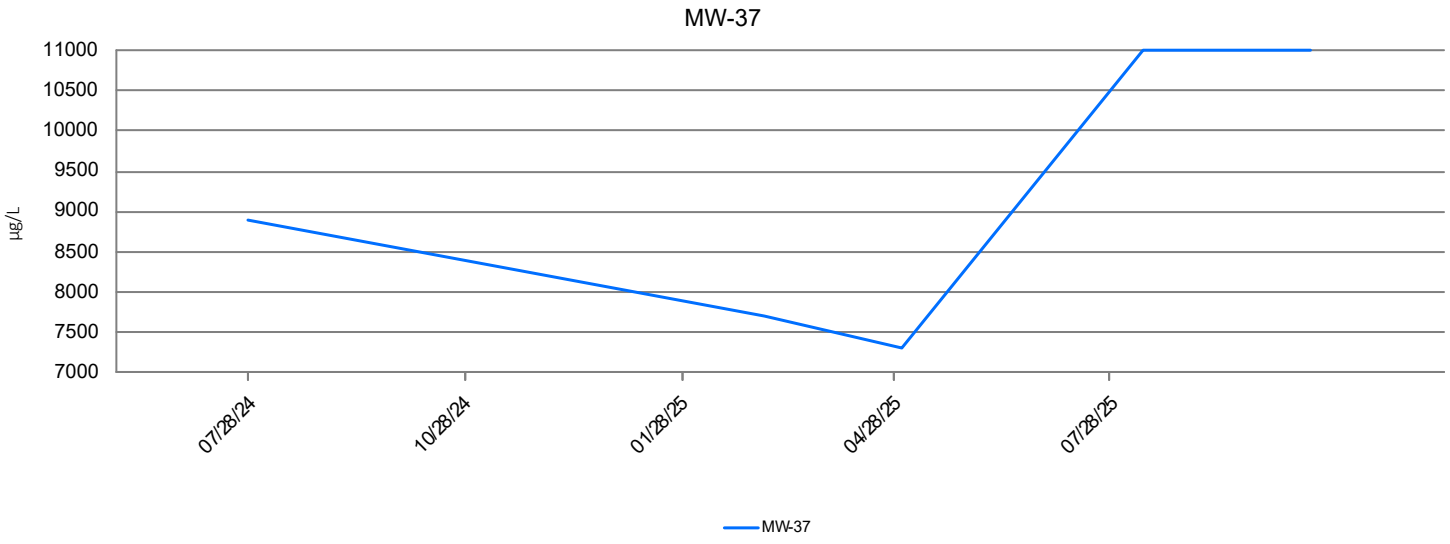


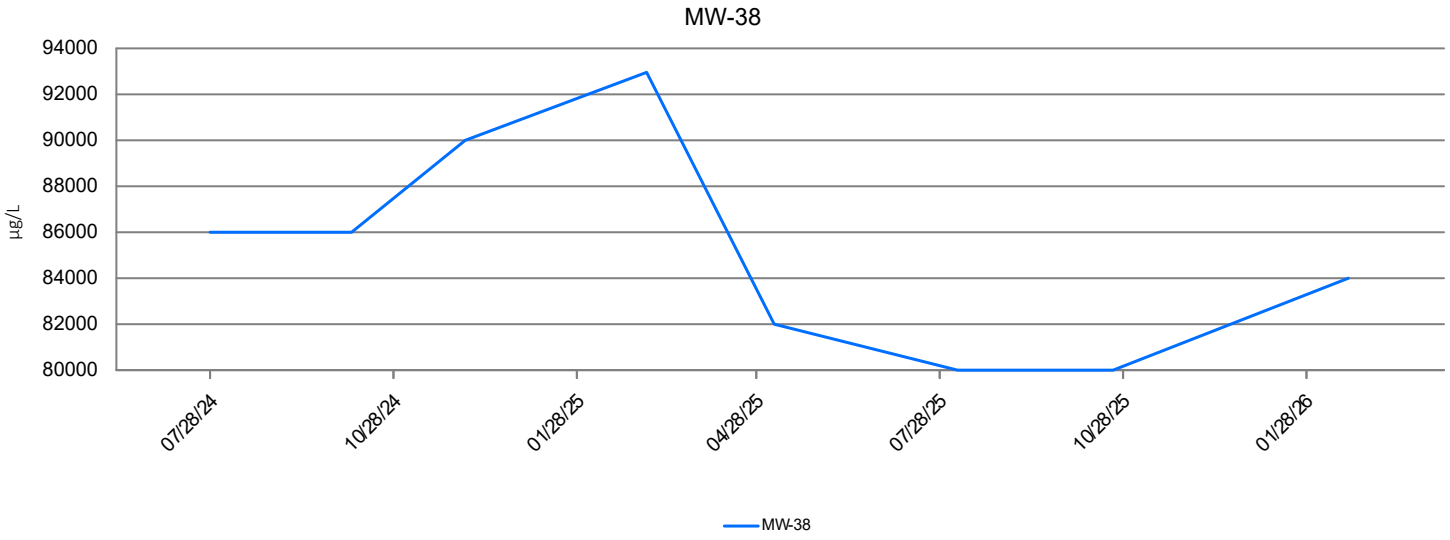
Variable Graphical Report

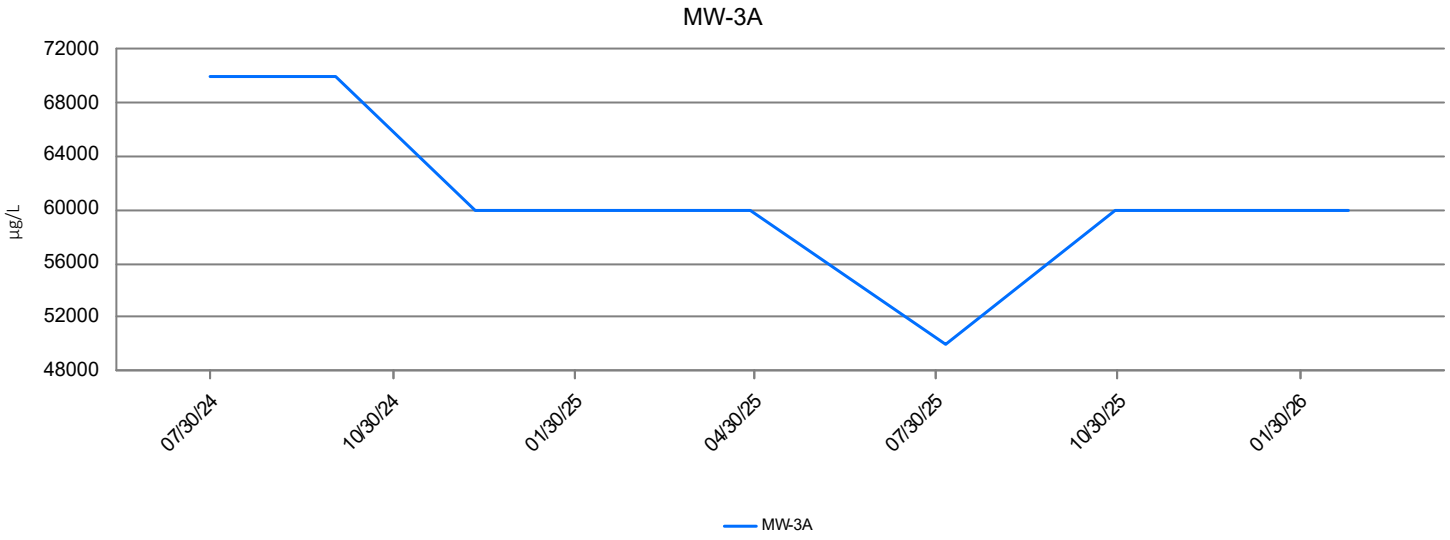
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sodium, Dissolved (µg/L)







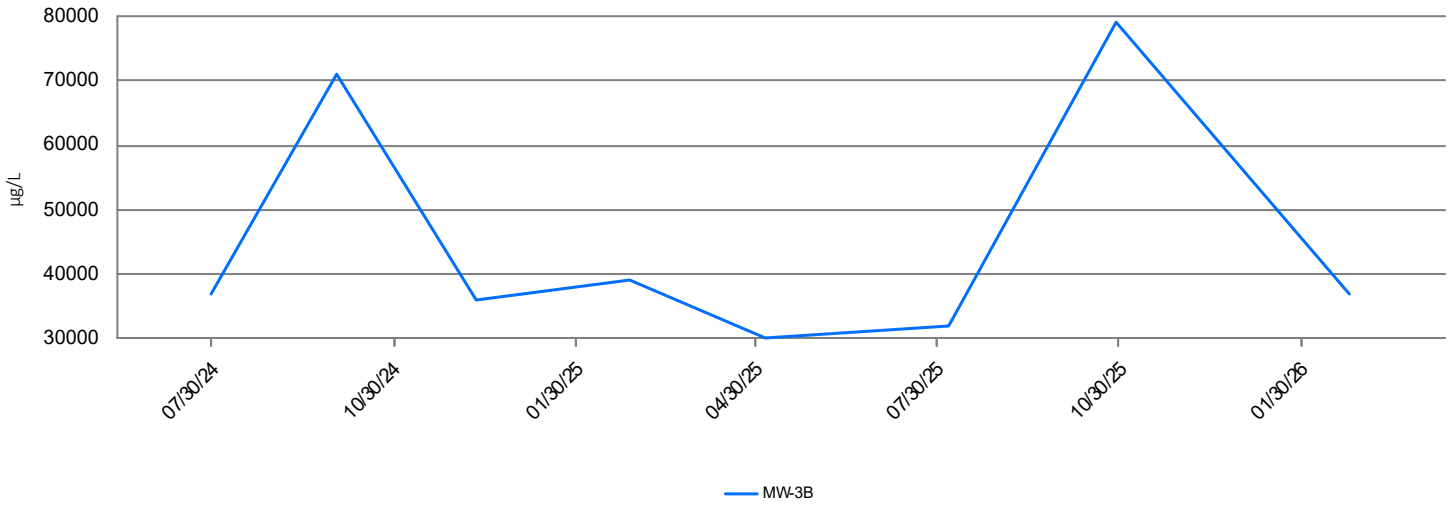
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

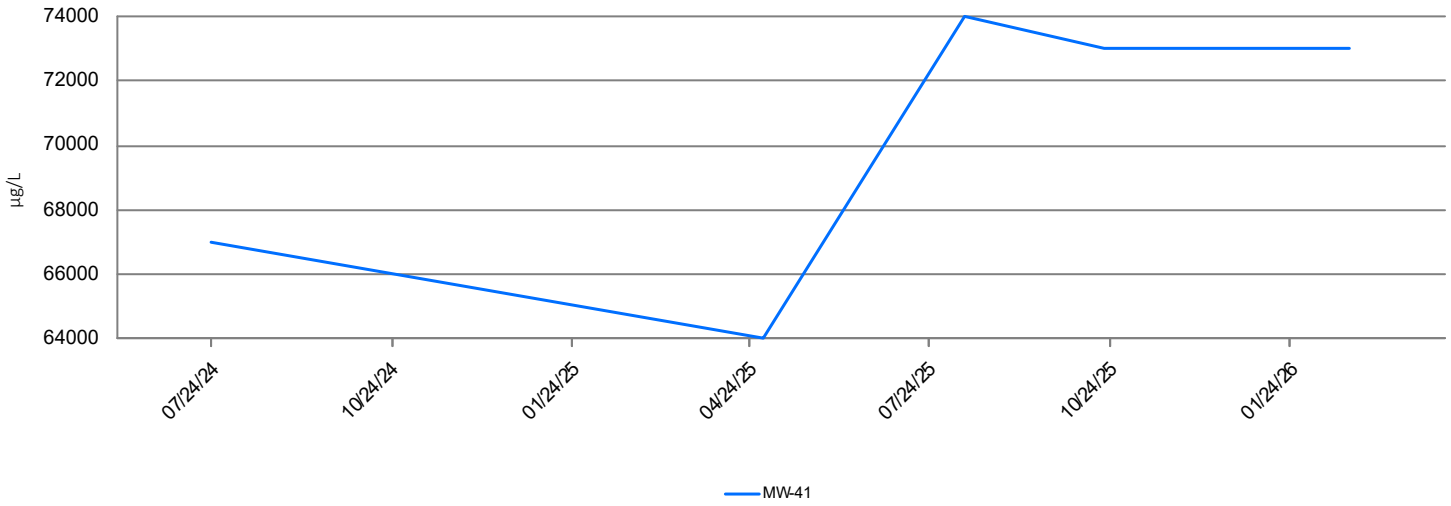
MonitorPro

No Group Selected, Sodium, Dissolved (µg/L)

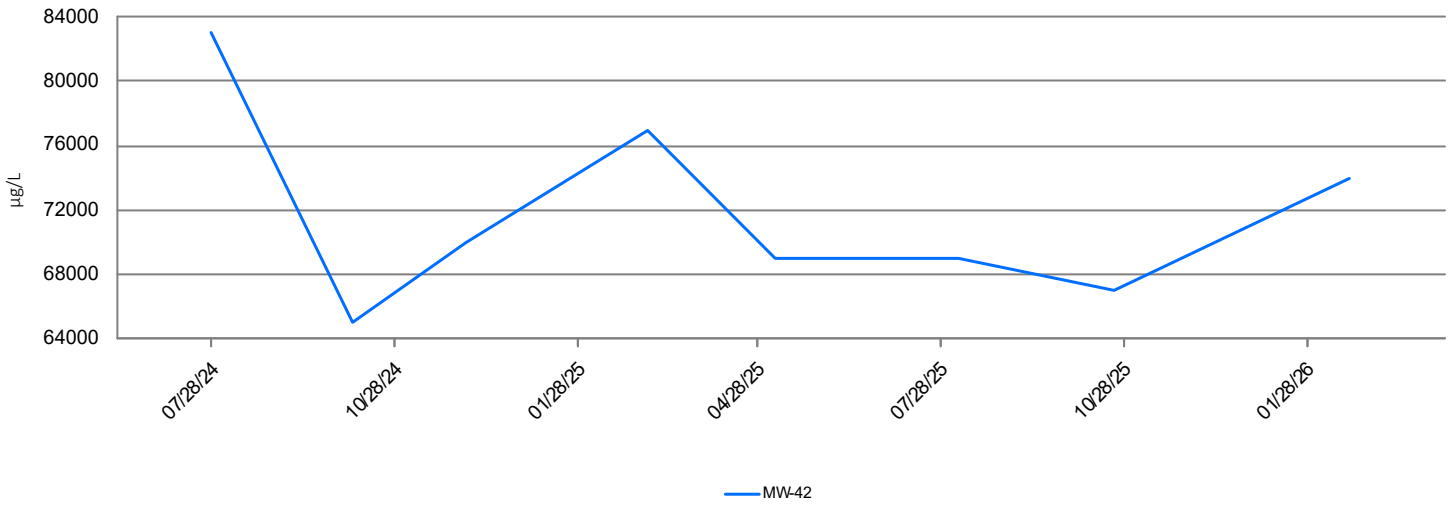
MW-3B



MW-41



MW-42

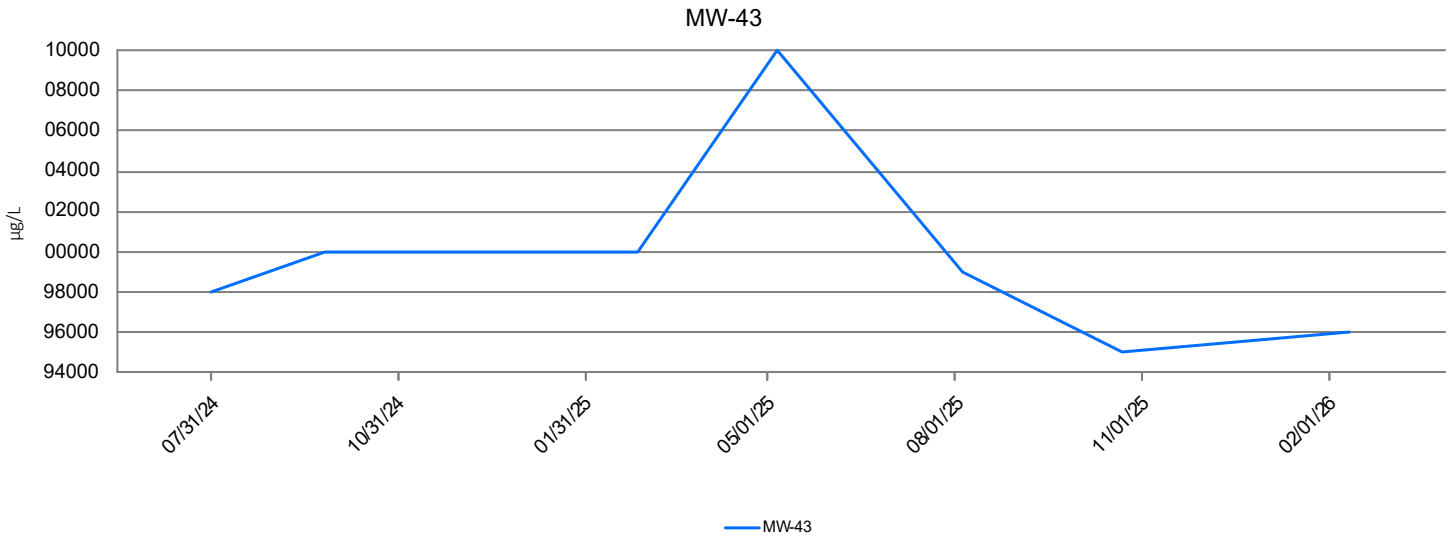


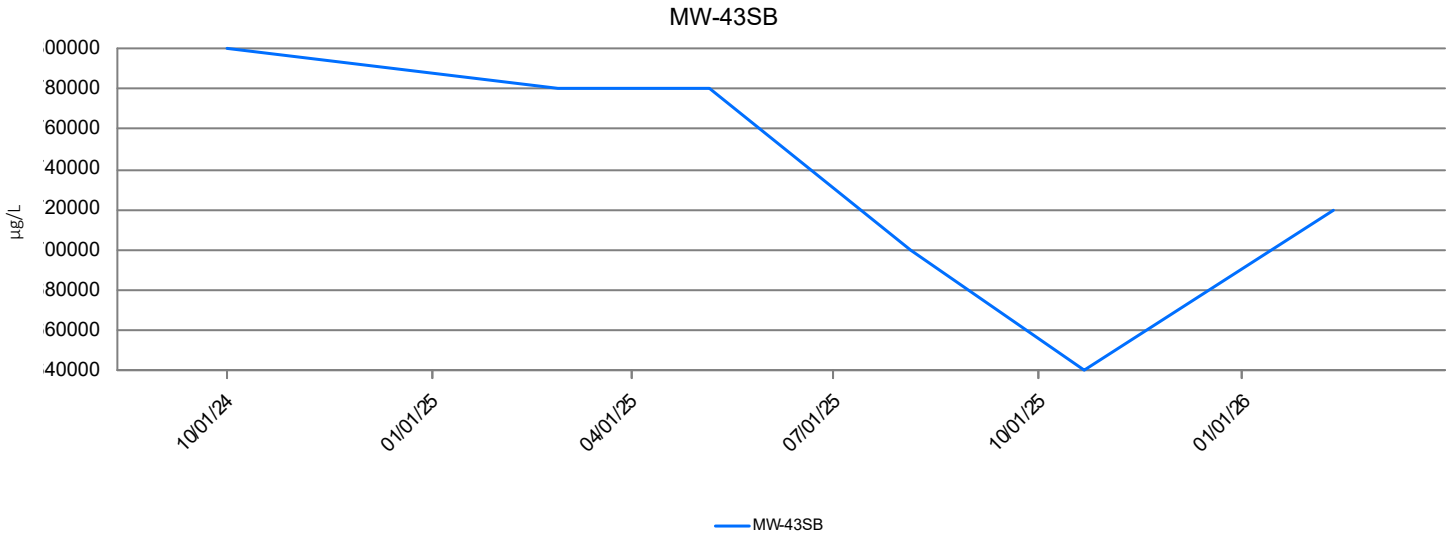
Variable Graphical Report

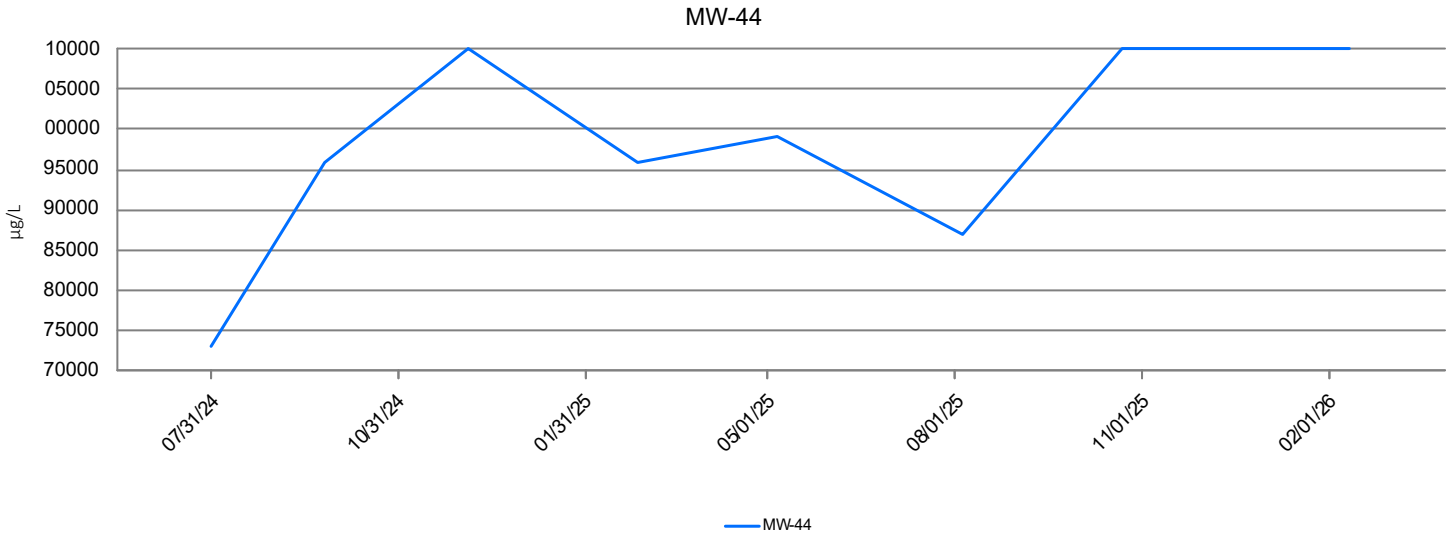
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sodium, Dissolved (µg/L)





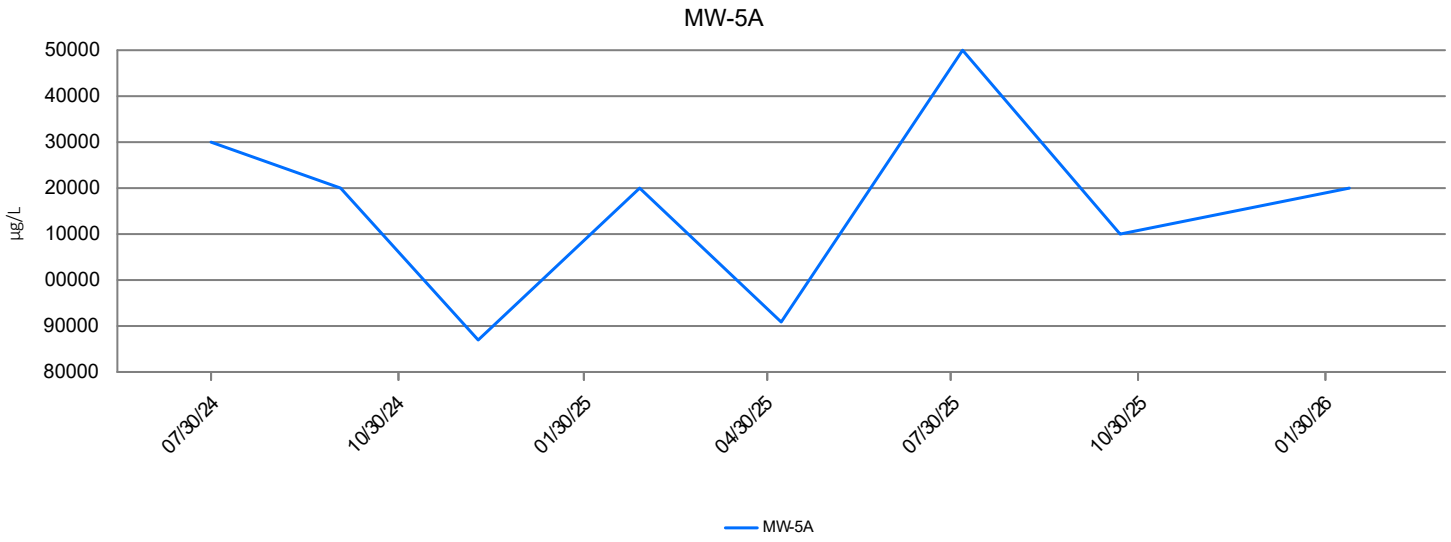


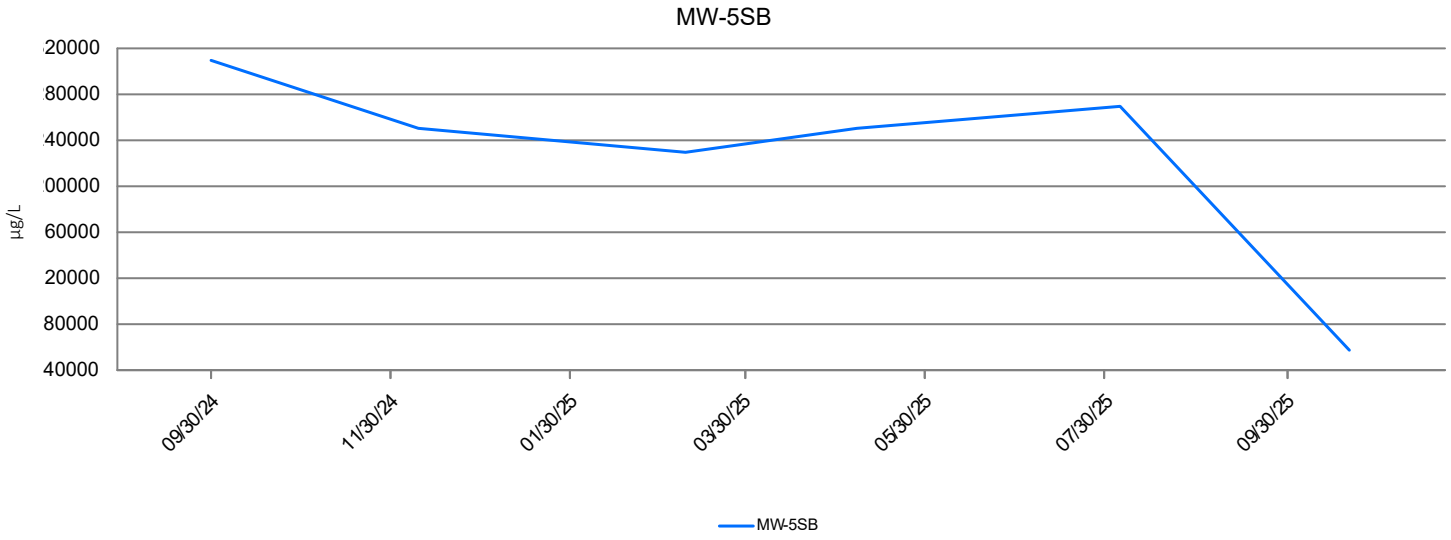
Variable Graphical Report

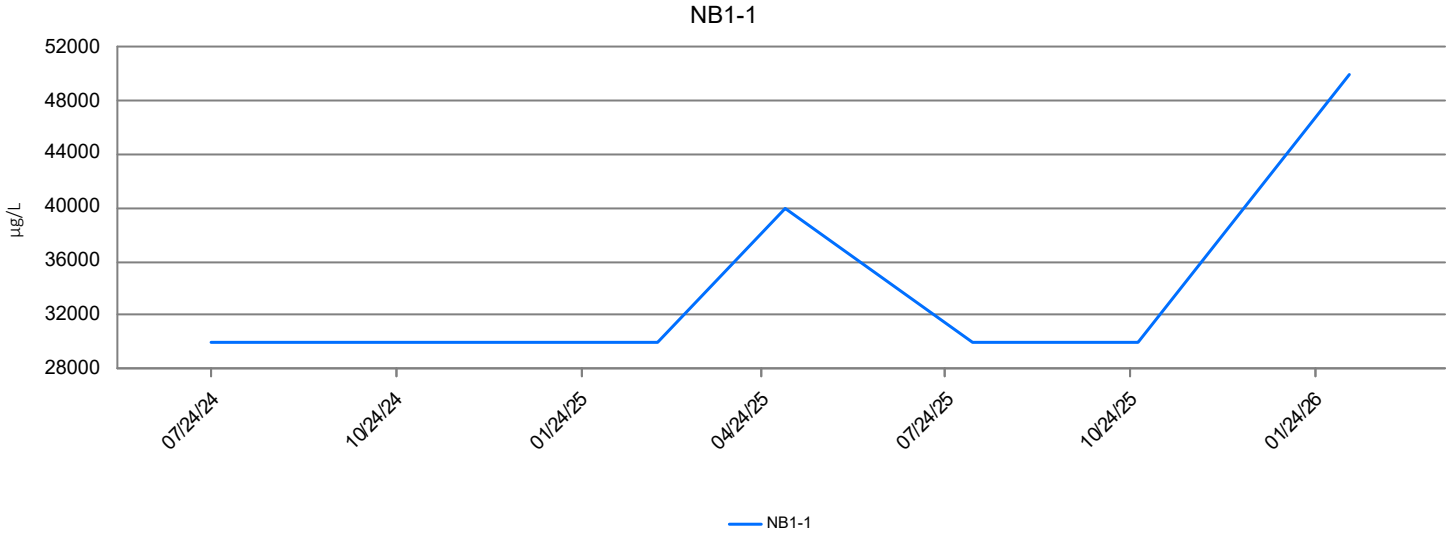
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sodium, Dissolved (µg/L)





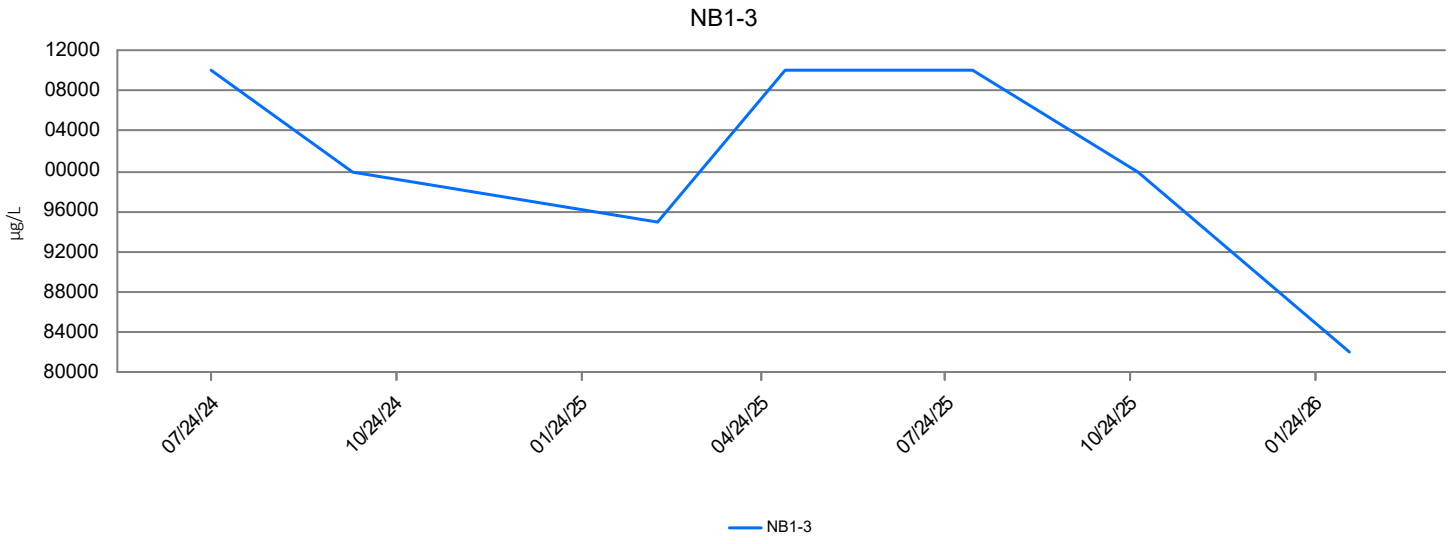


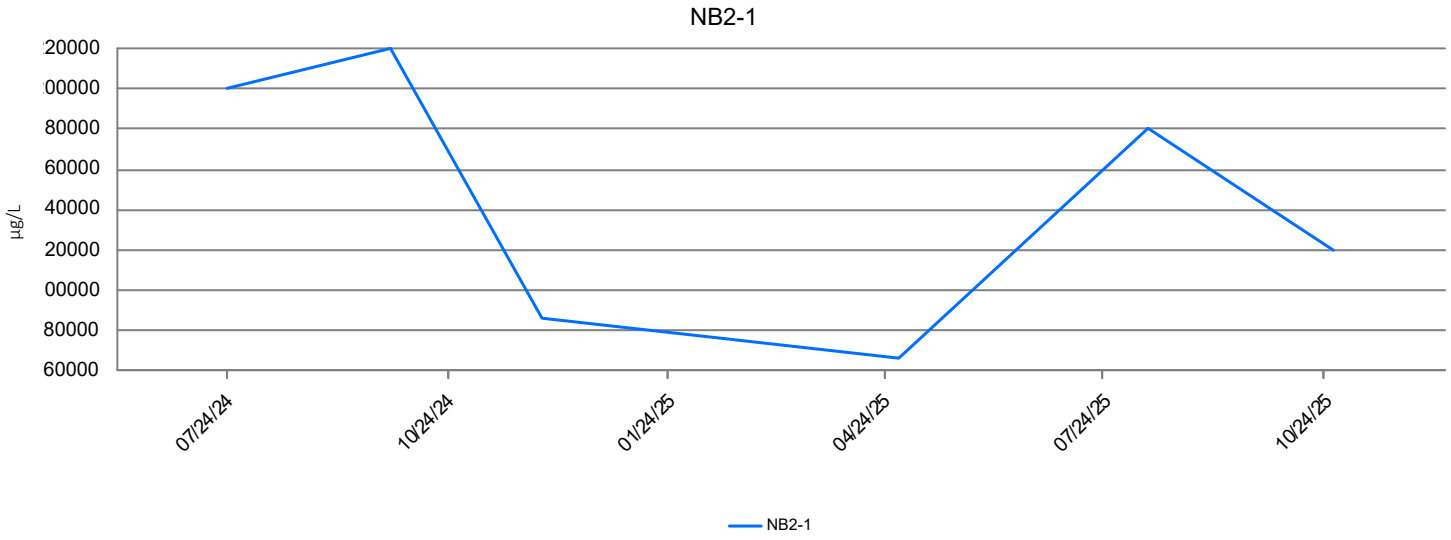
Variable Graphical Report

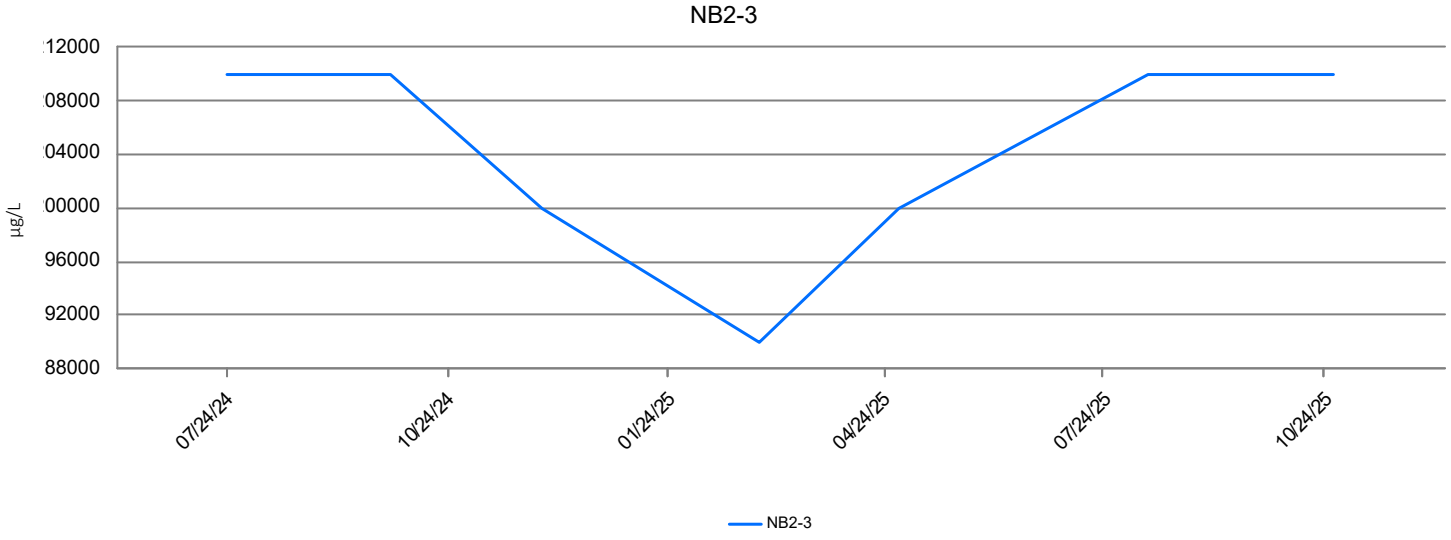
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sodium, Dissolved (µg/L)





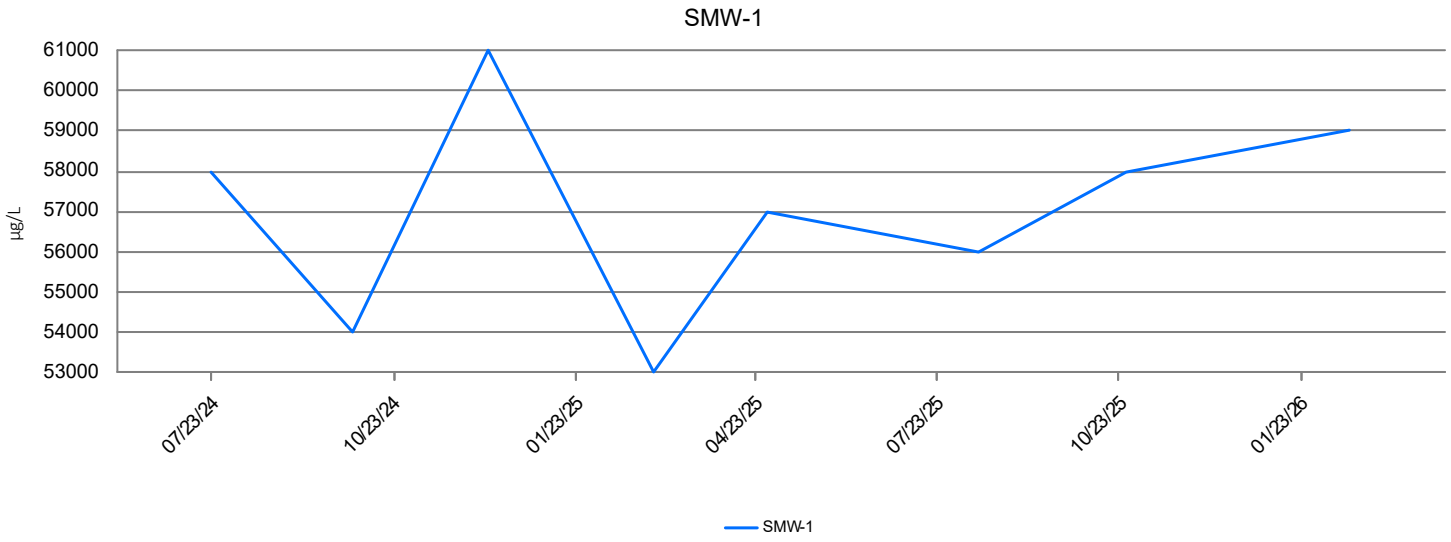


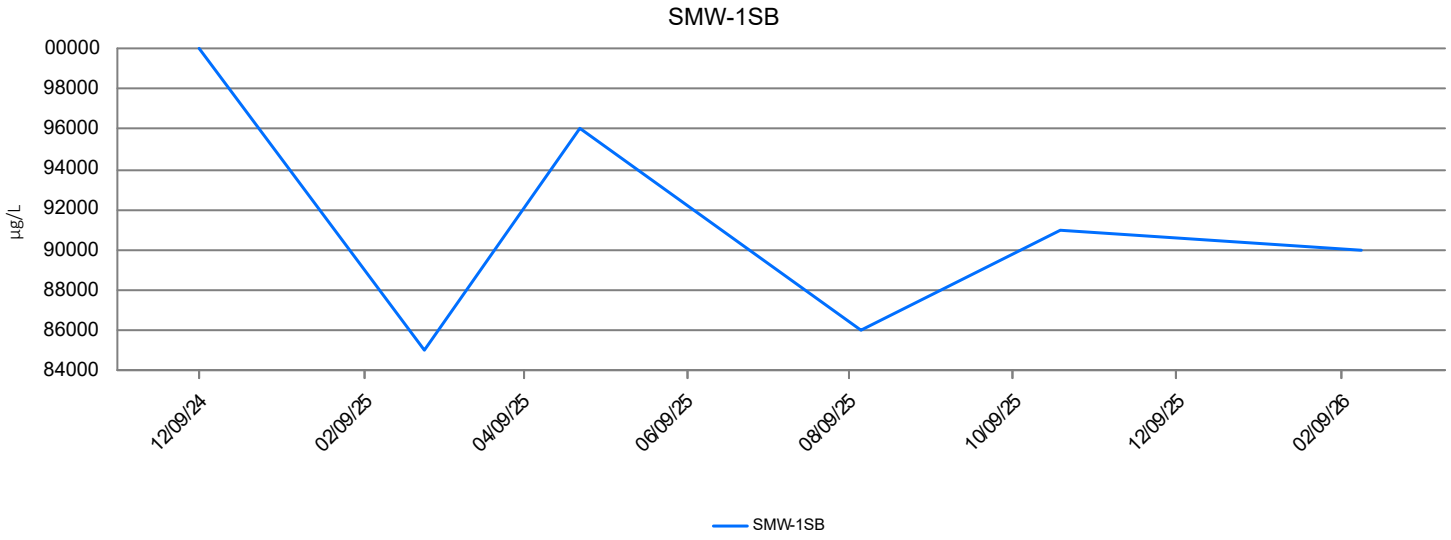
Variable Graphical Report

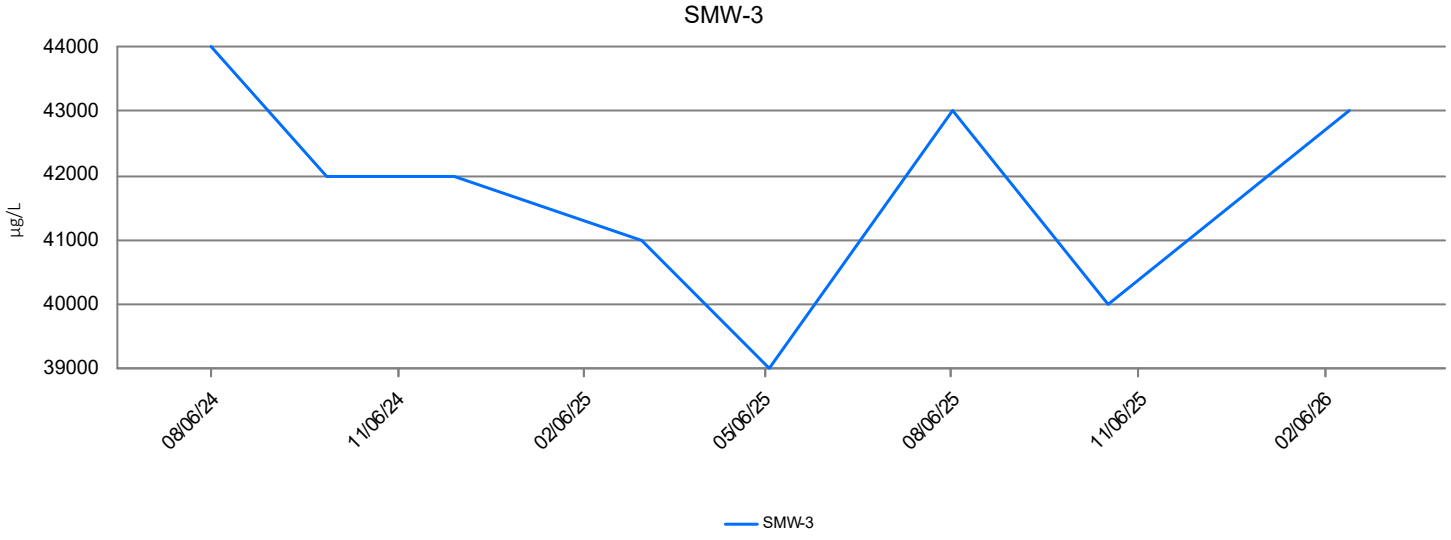
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sodium, Dissolved (µg/L)







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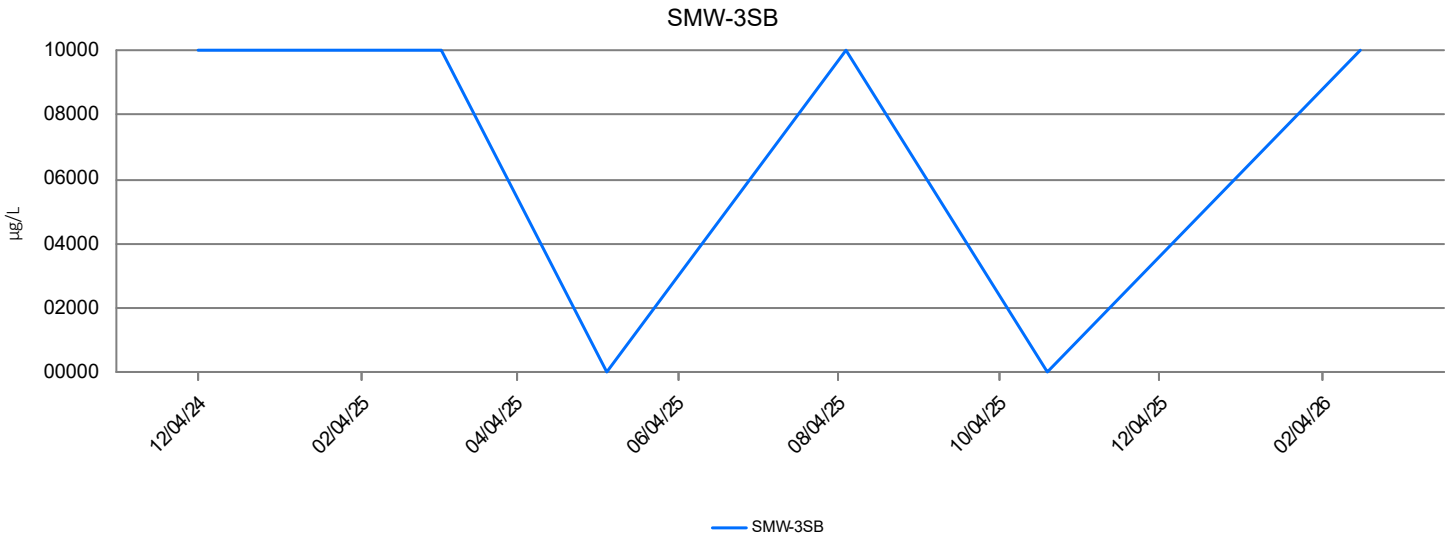
MCERTS

Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sodium, Dissolved (µg/L)

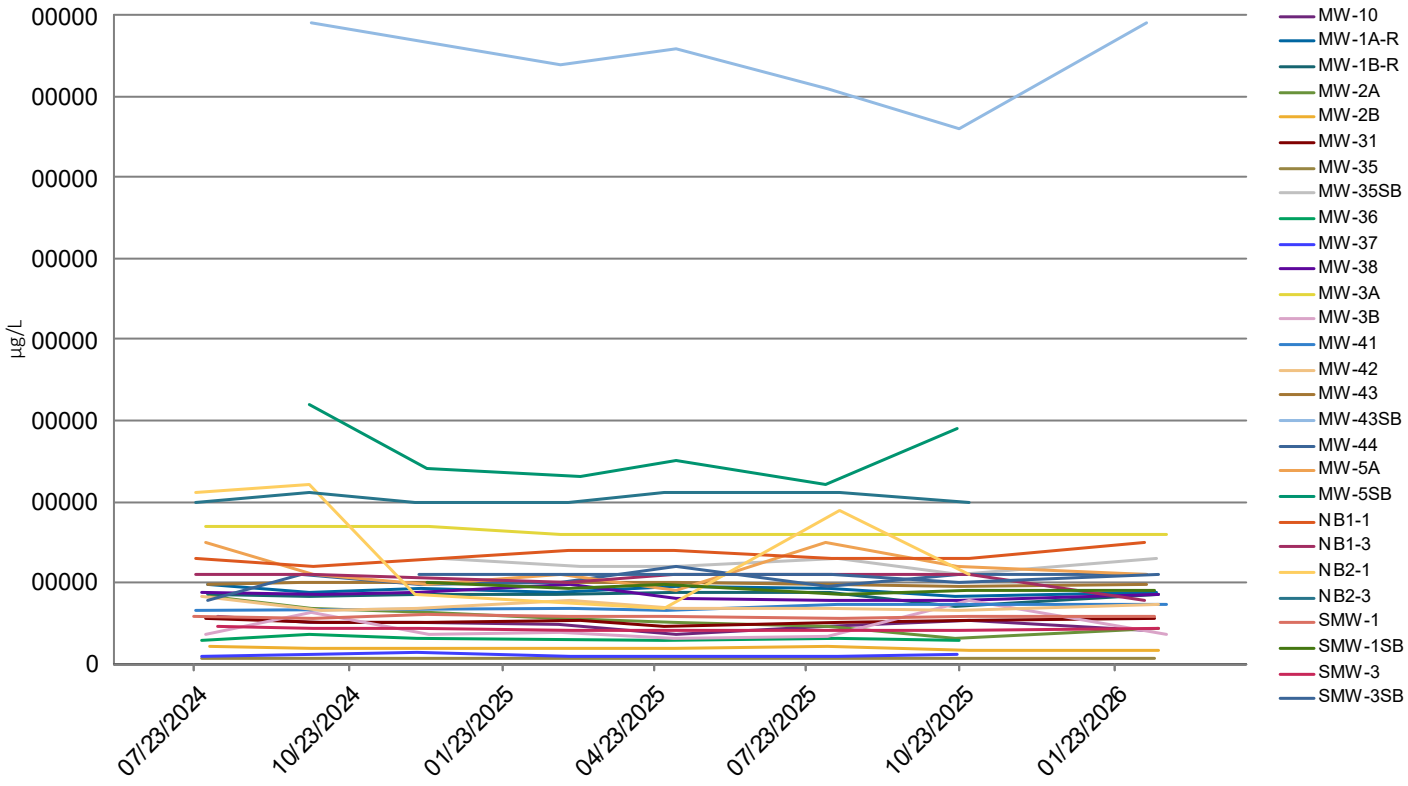


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sodium, Total Recoverable (µg/L)

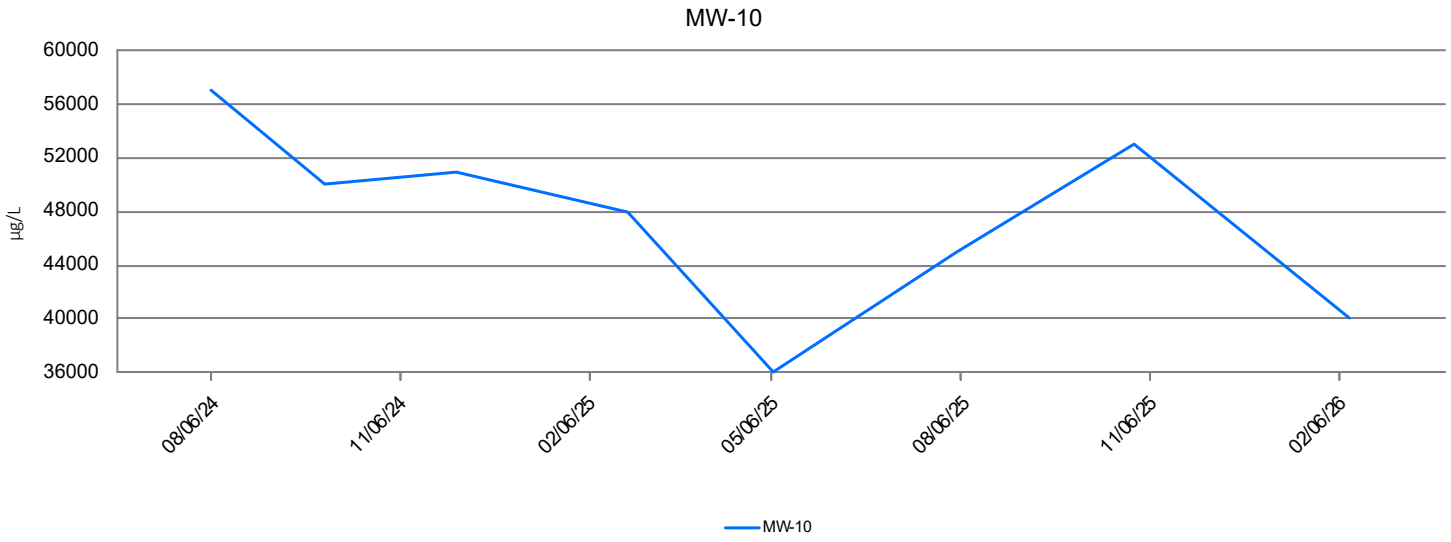


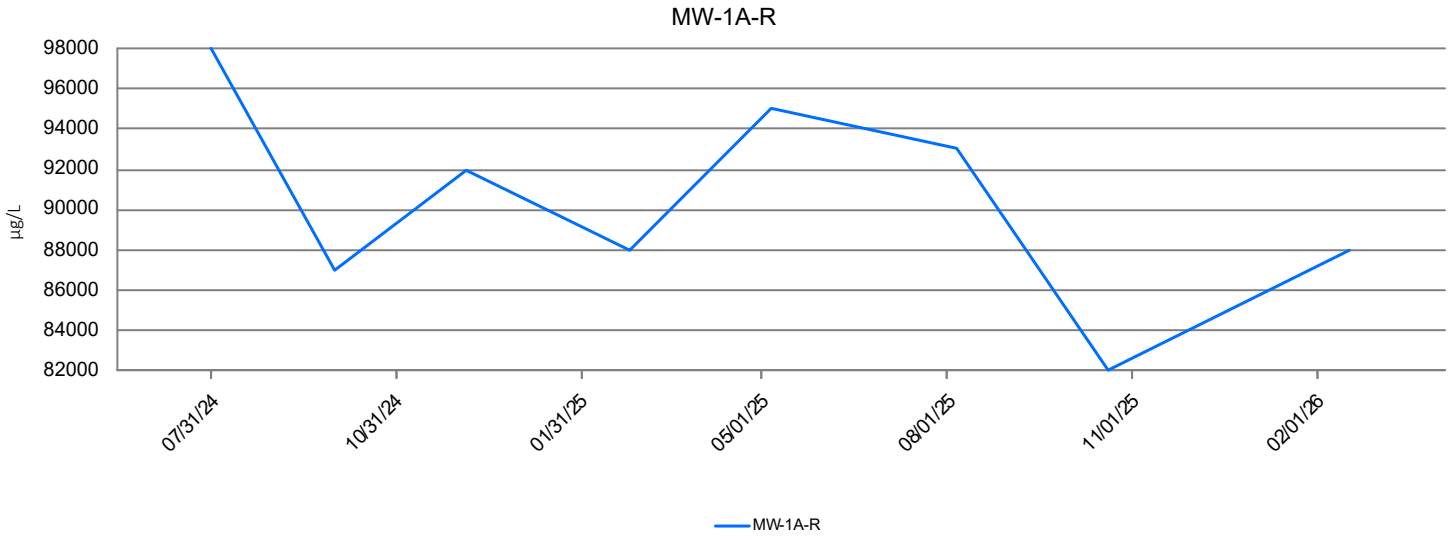
Variable Graphical Report

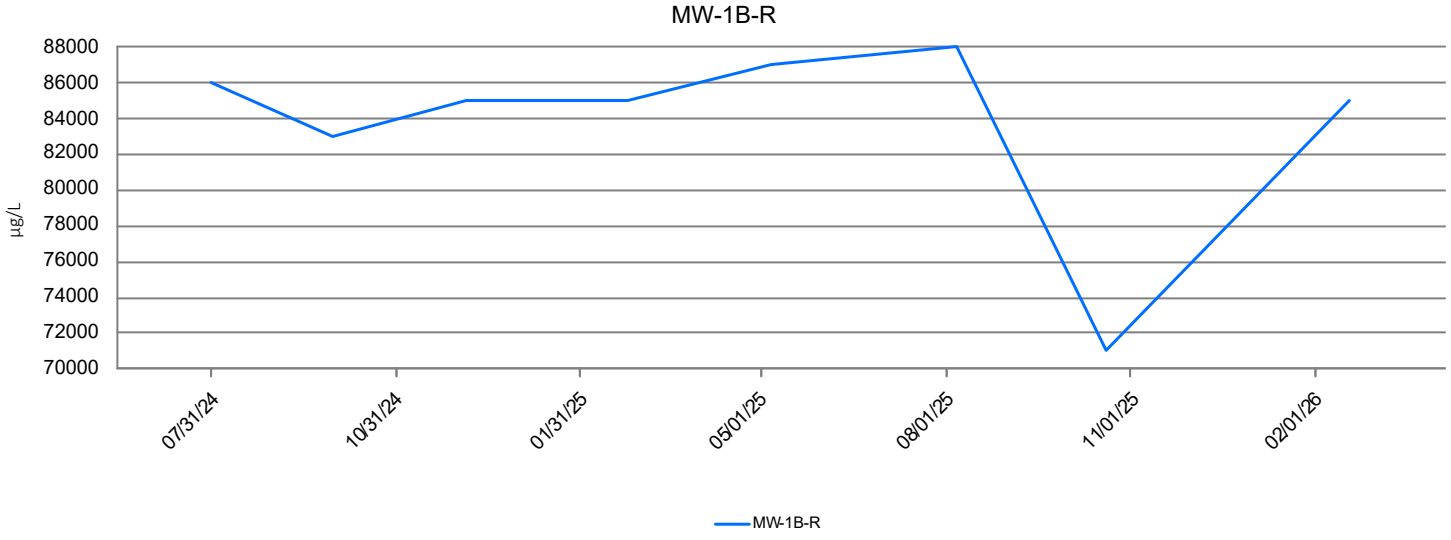
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sodium, Total Recoverable (µg/L)







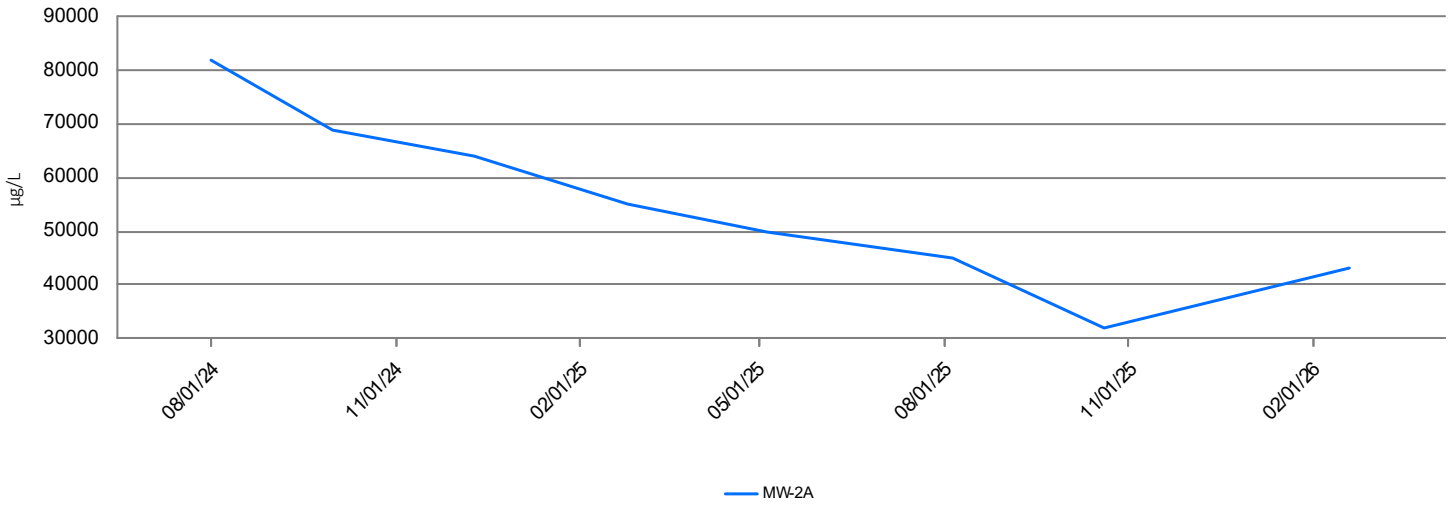
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

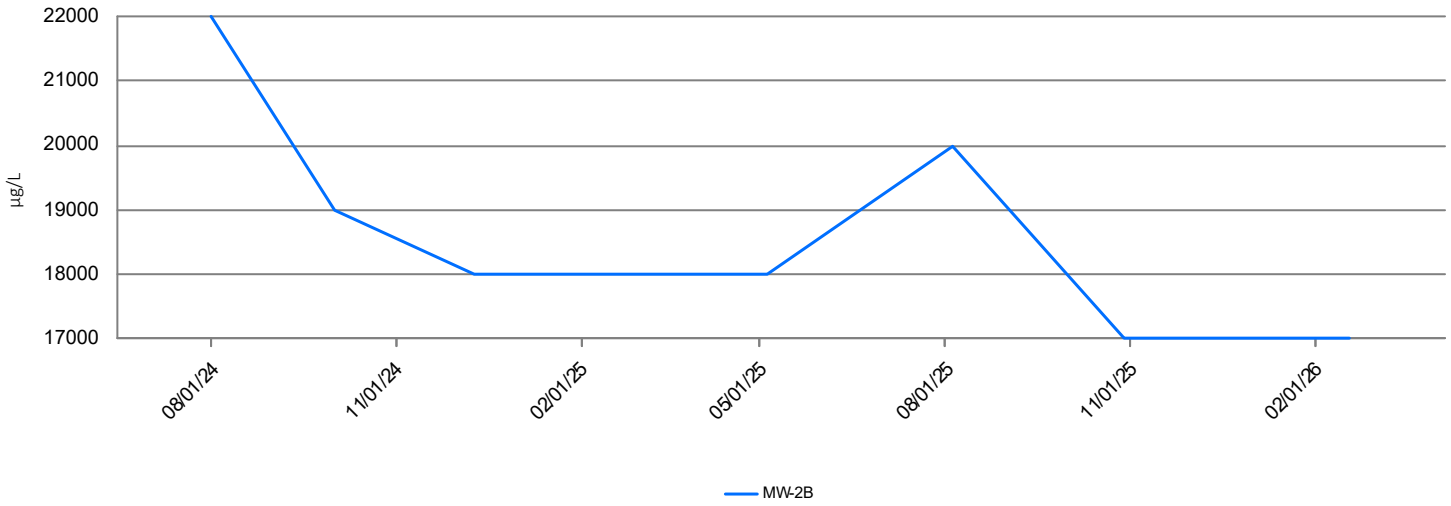
MonitorPro

No Group Selected, Sodium, Total Recoverable (µg/L)

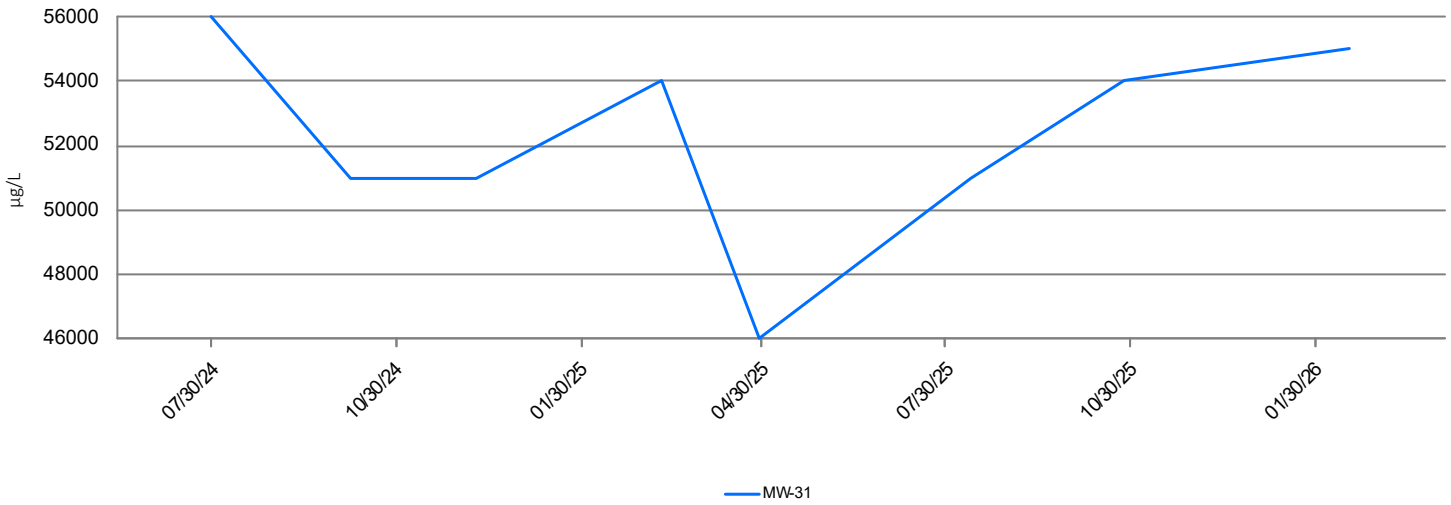
MW-2A



MW-2B



MW-31



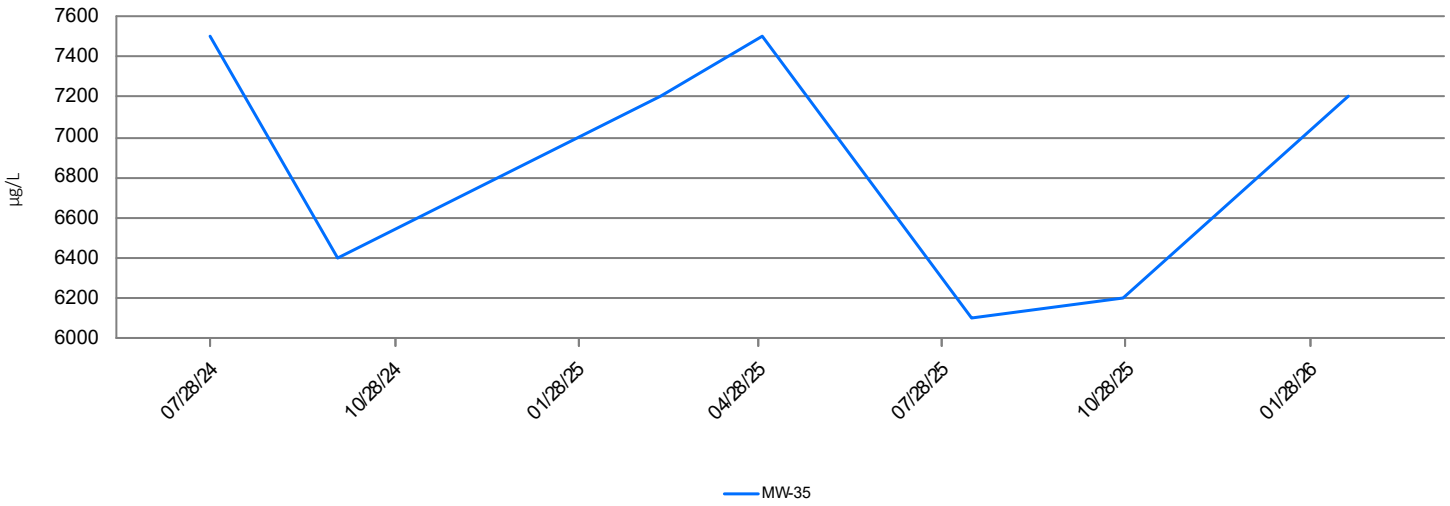
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

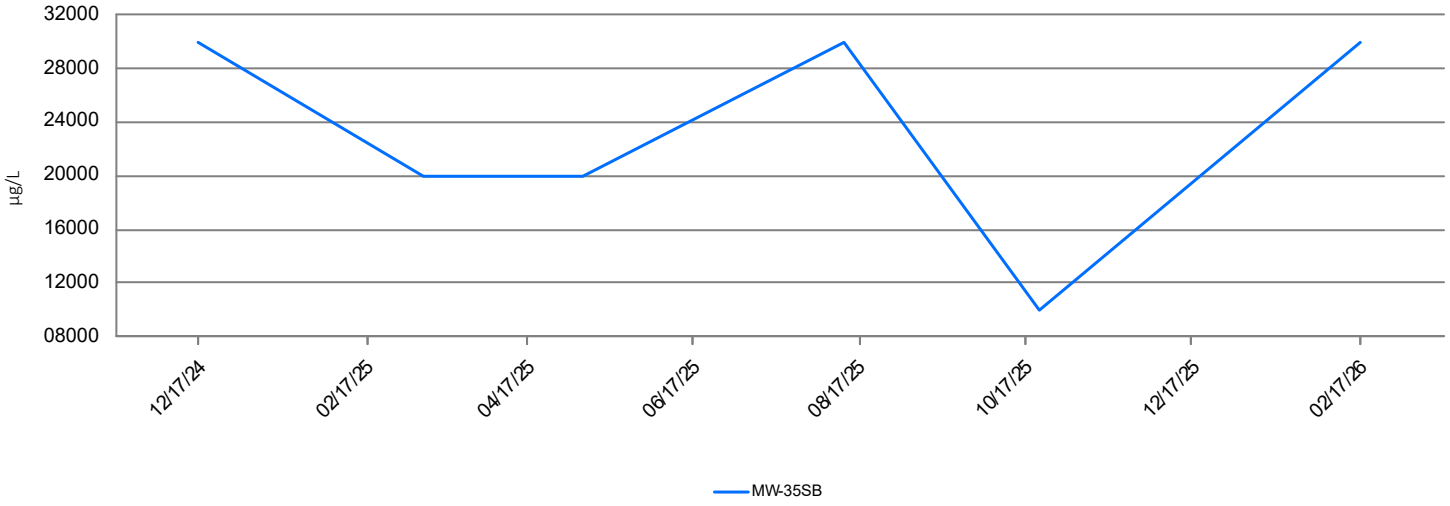
MonitorPro

No Group Selected, Sodium, Total Recoverable (µg/L)

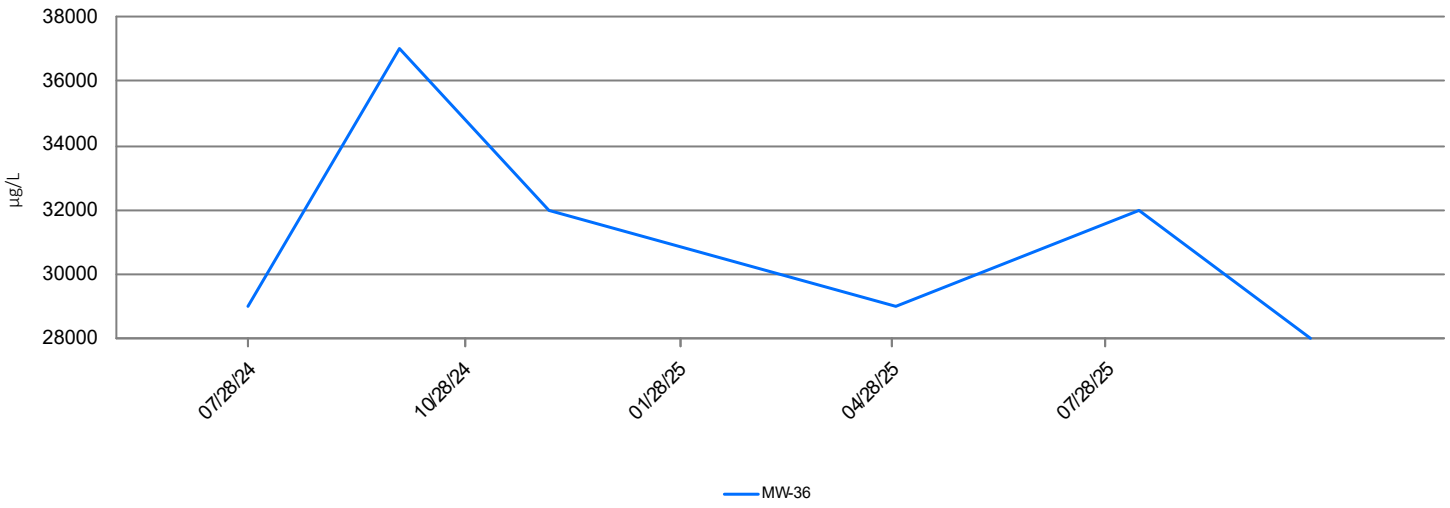
MW-35



MW-35SB



MW-36



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EHS DATA

MCERTS Cert. no. Sira MC090140/02

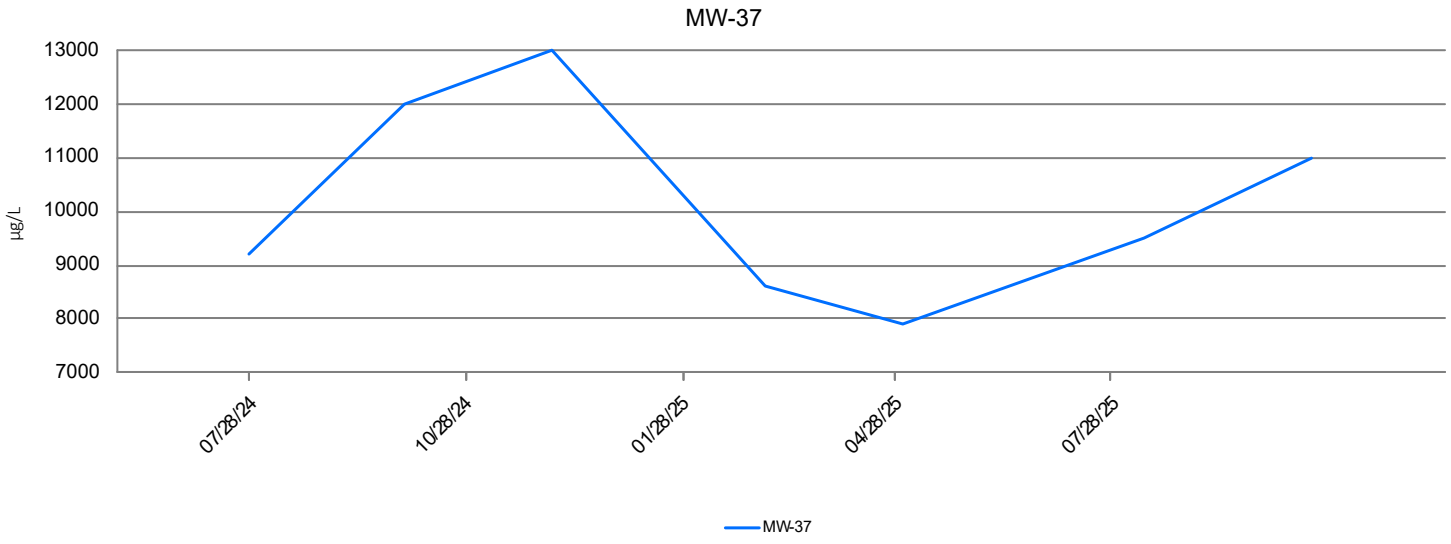
MCERTS

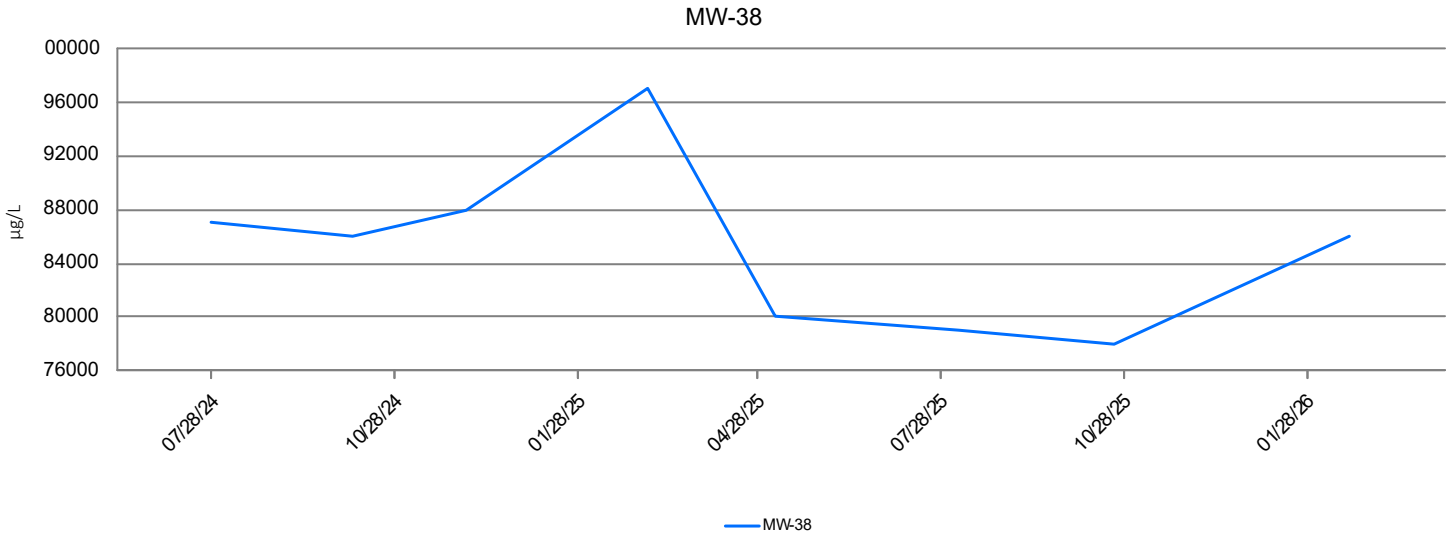
Variable Graphical Report

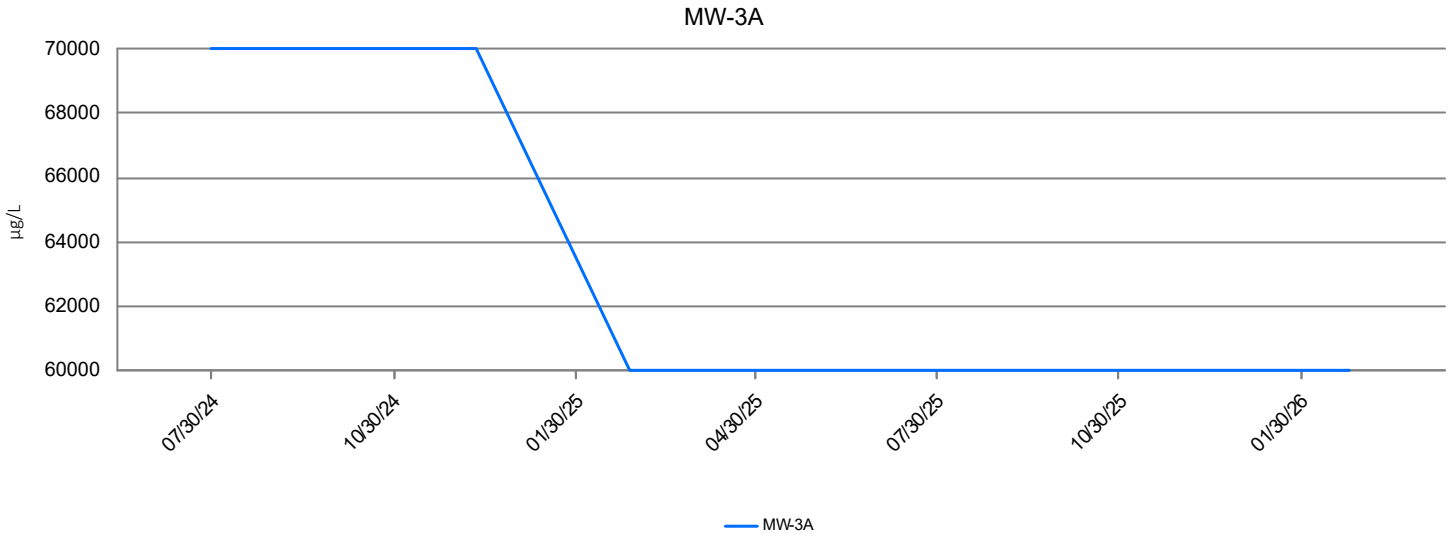
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sodium, Total Recoverable (µg/L)





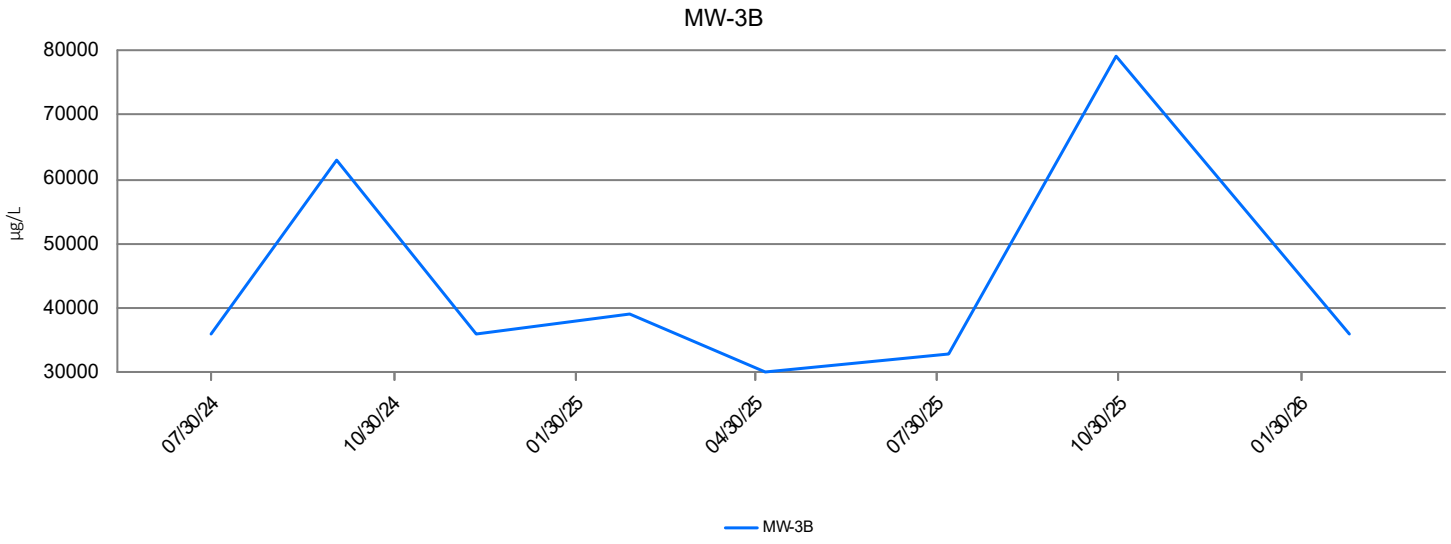


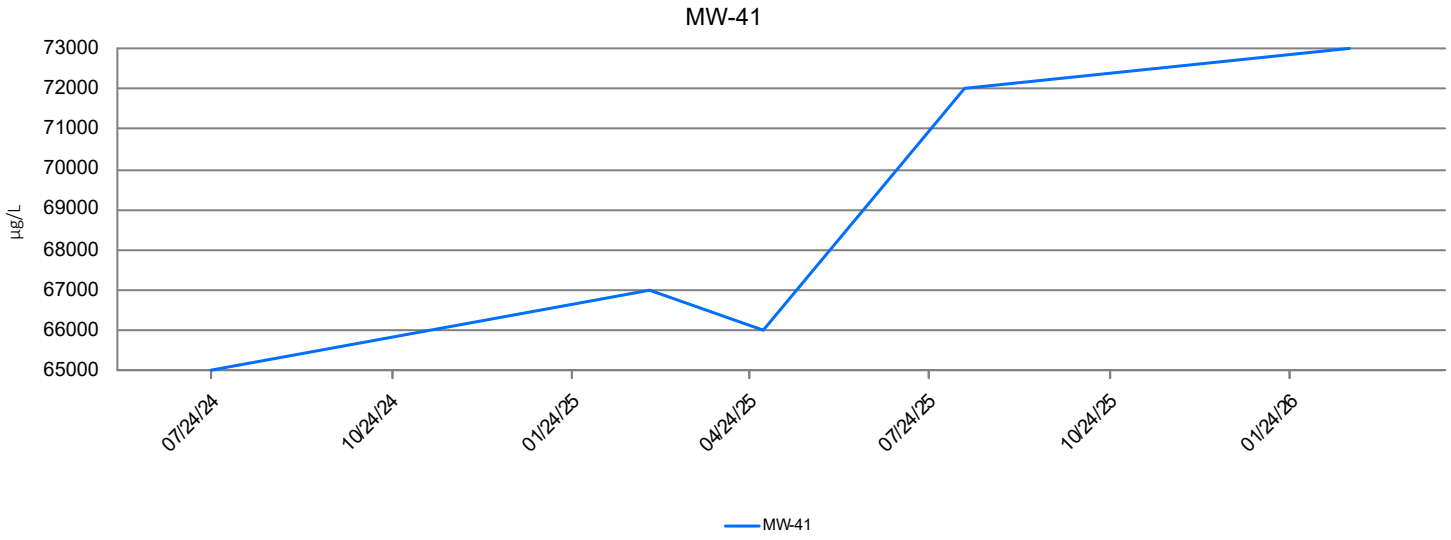
Variable Graphical Report

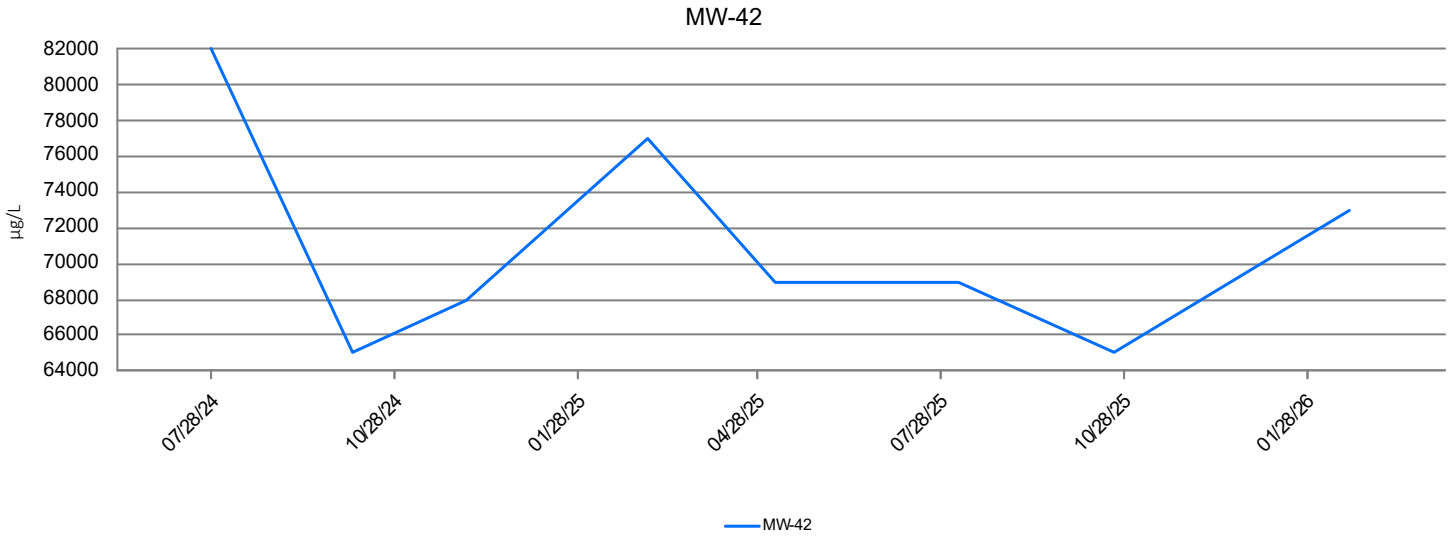
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sodium, Total Recoverable (µg/L)







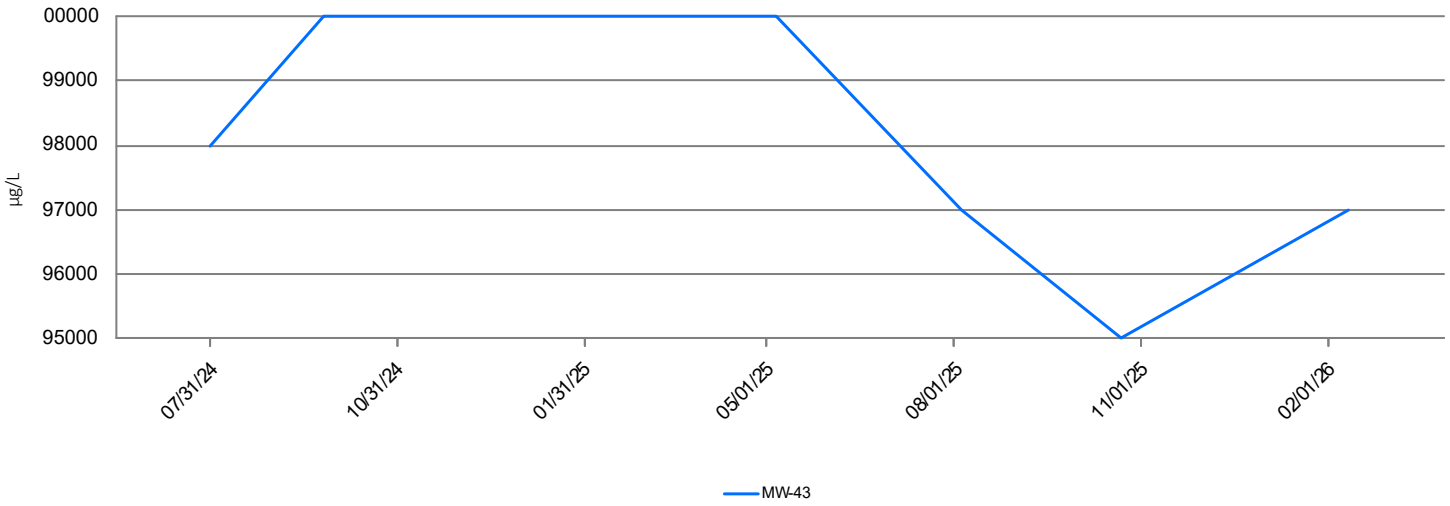
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

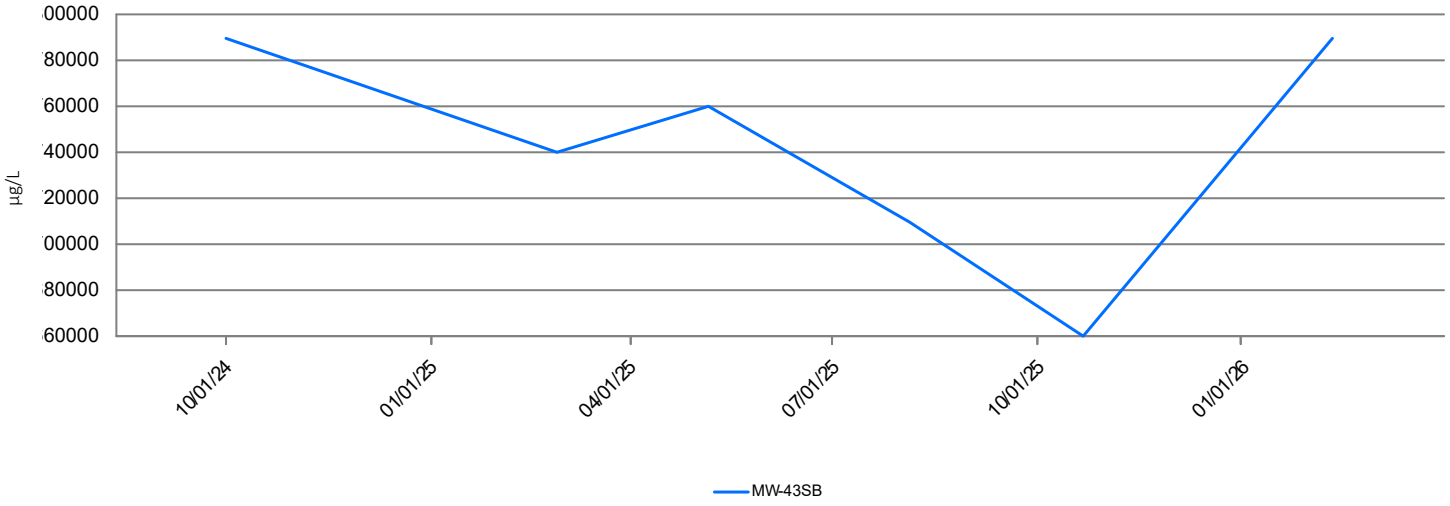
MonitorPro

No Group Selected, Sodium, Total Recoverable (µg/L)

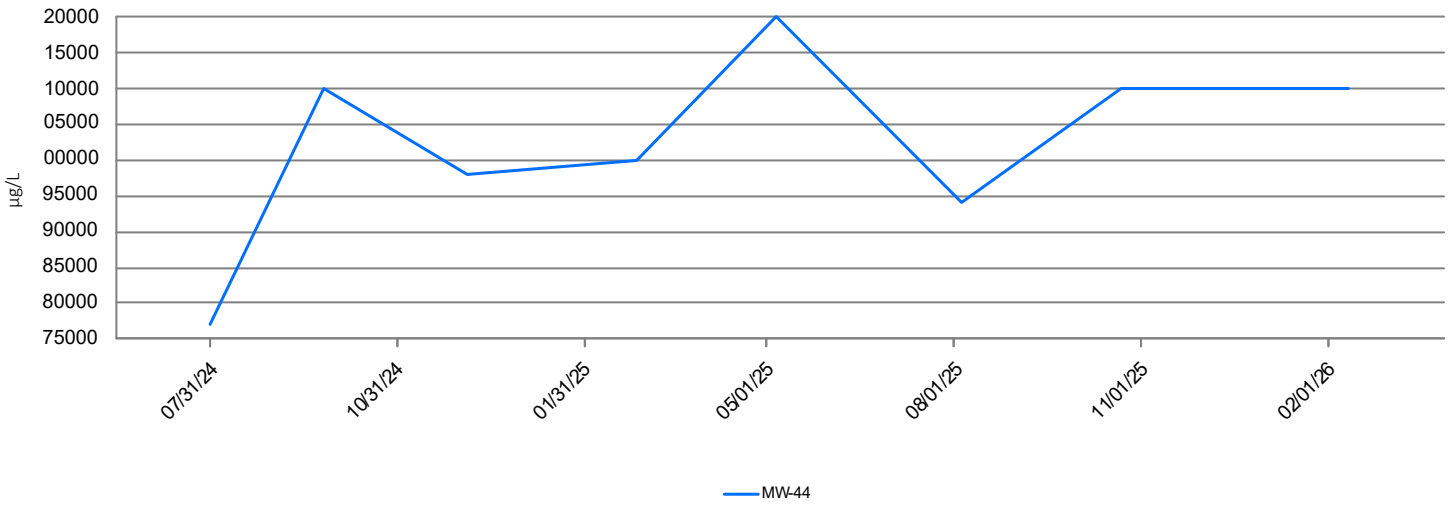
MW-43



MW-43SB



MW-44



Printed Date: 05/21/2026

EHS DATA

MCERTS Cert. no. Sira MC090140/02

MCERTS

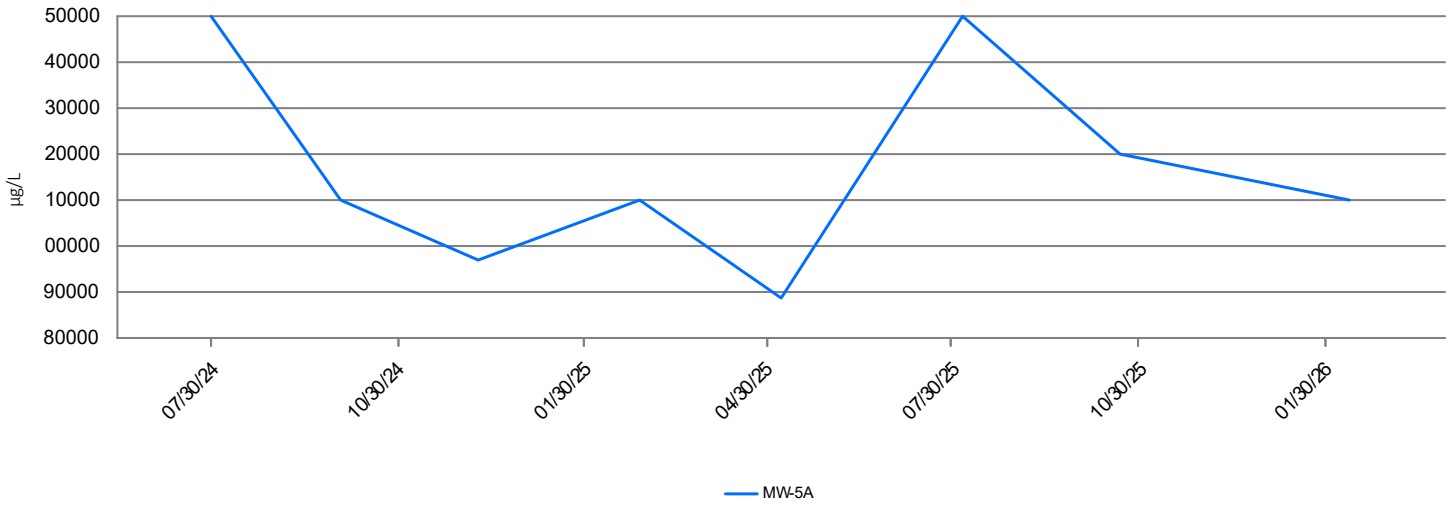
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Date from 07/01/2024 to 05/01/2026

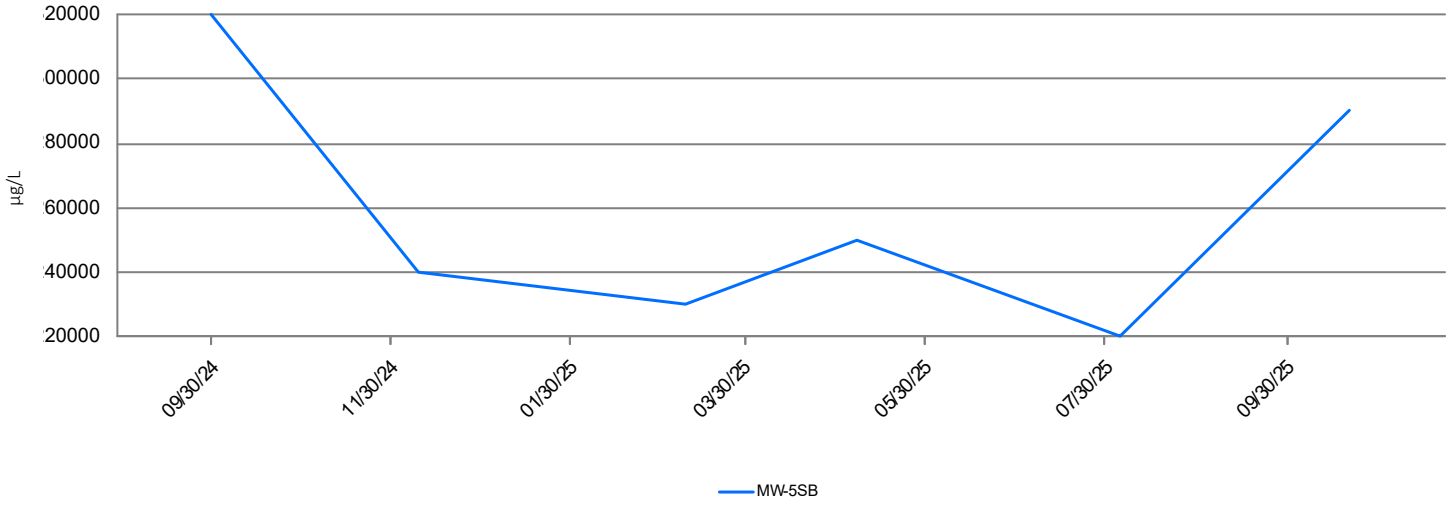
MonitorPro

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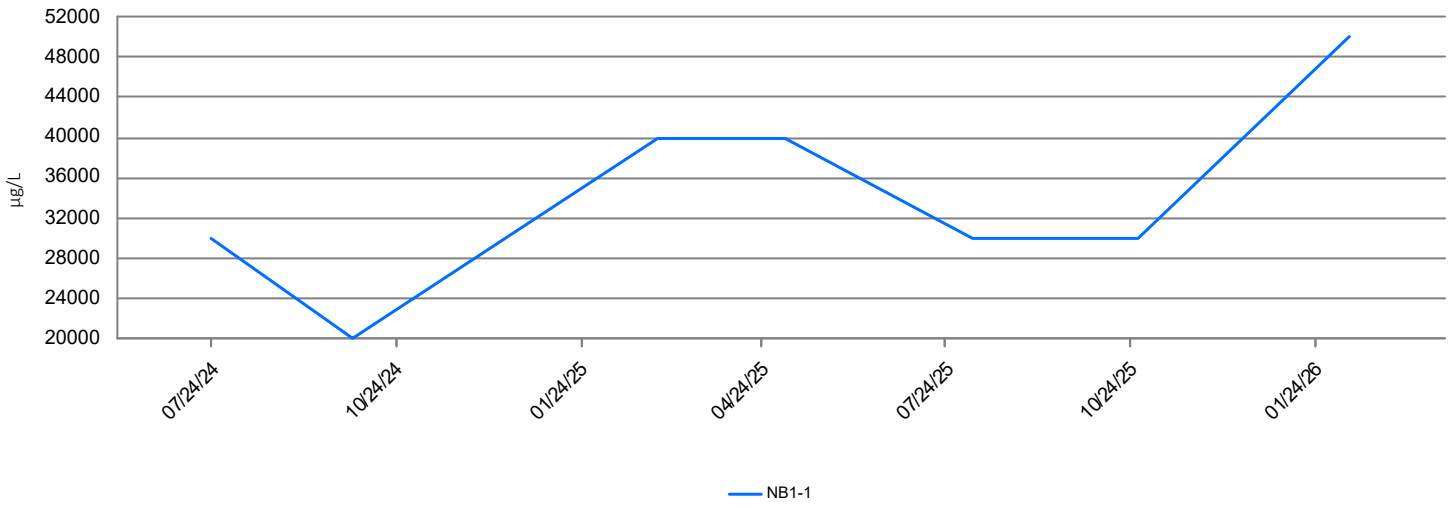
MW-5A



MW-5SB



NB1-1

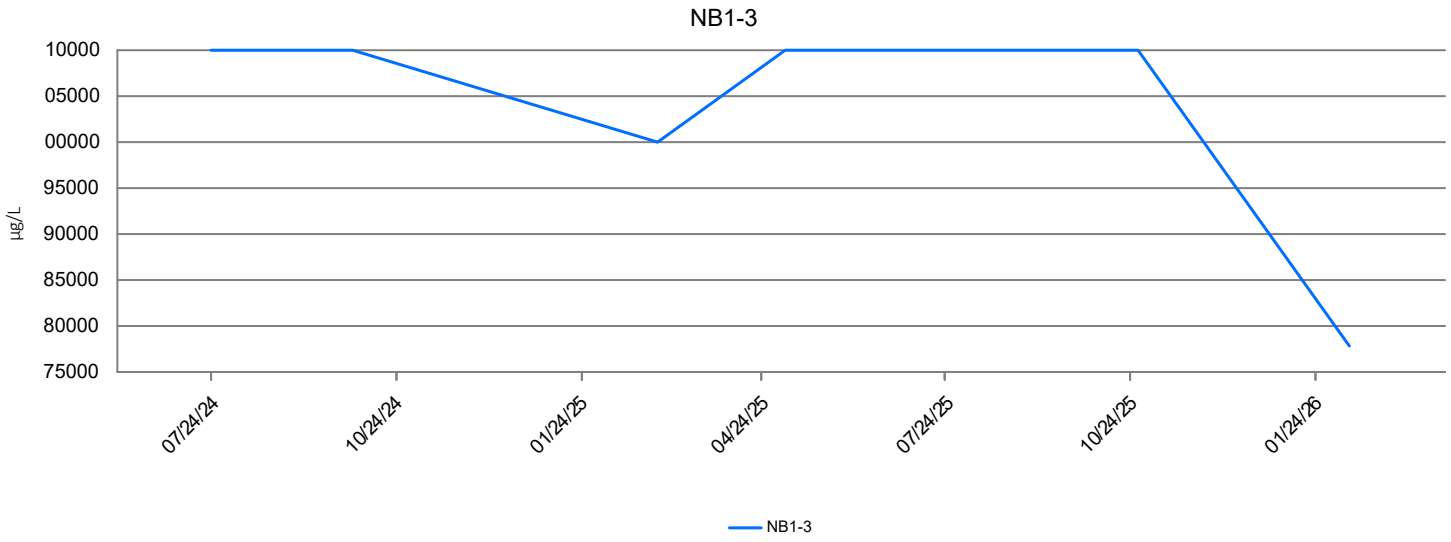


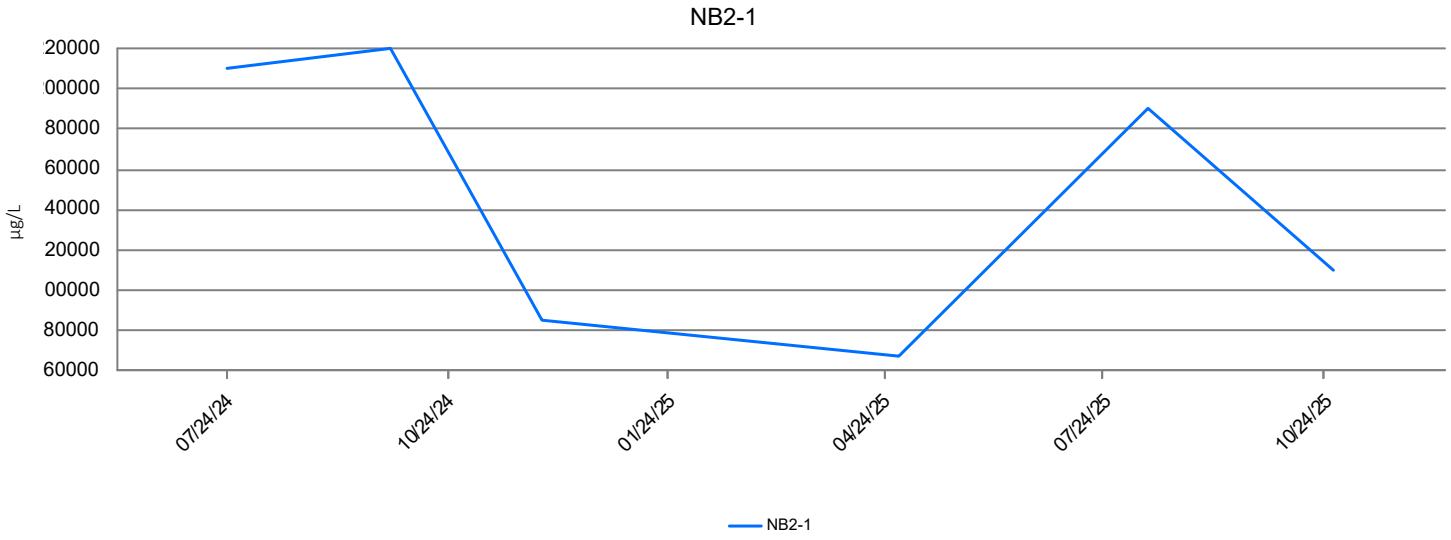
Variable Graphical Report

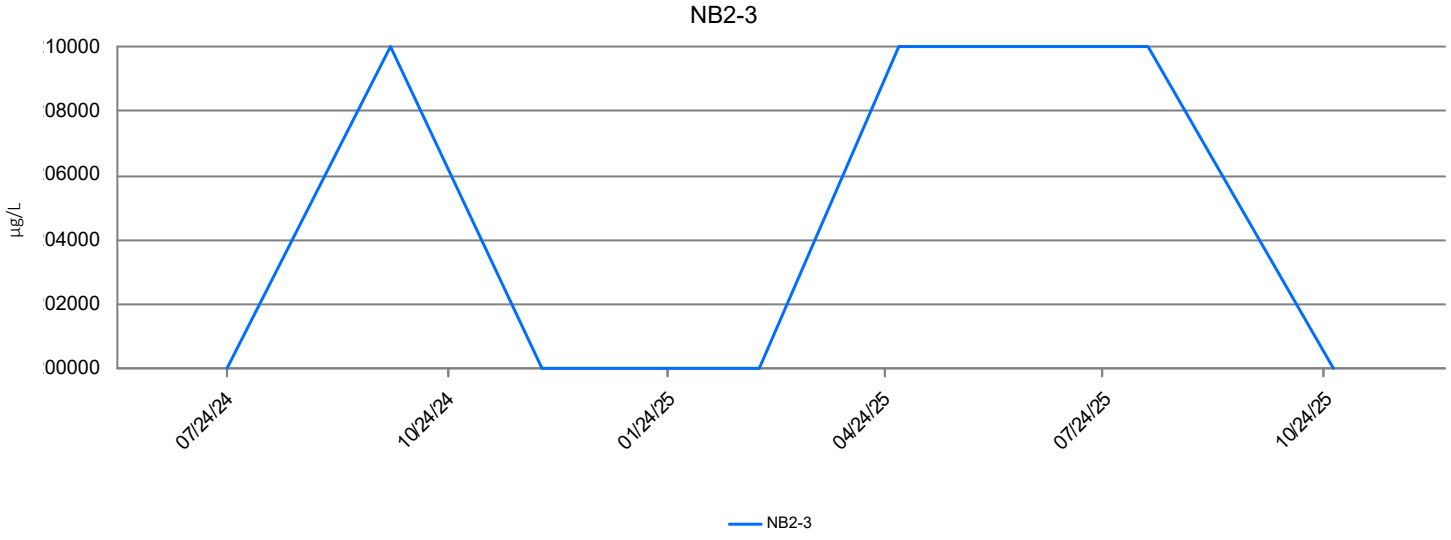
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sodium, Total Recoverable (µg/L)







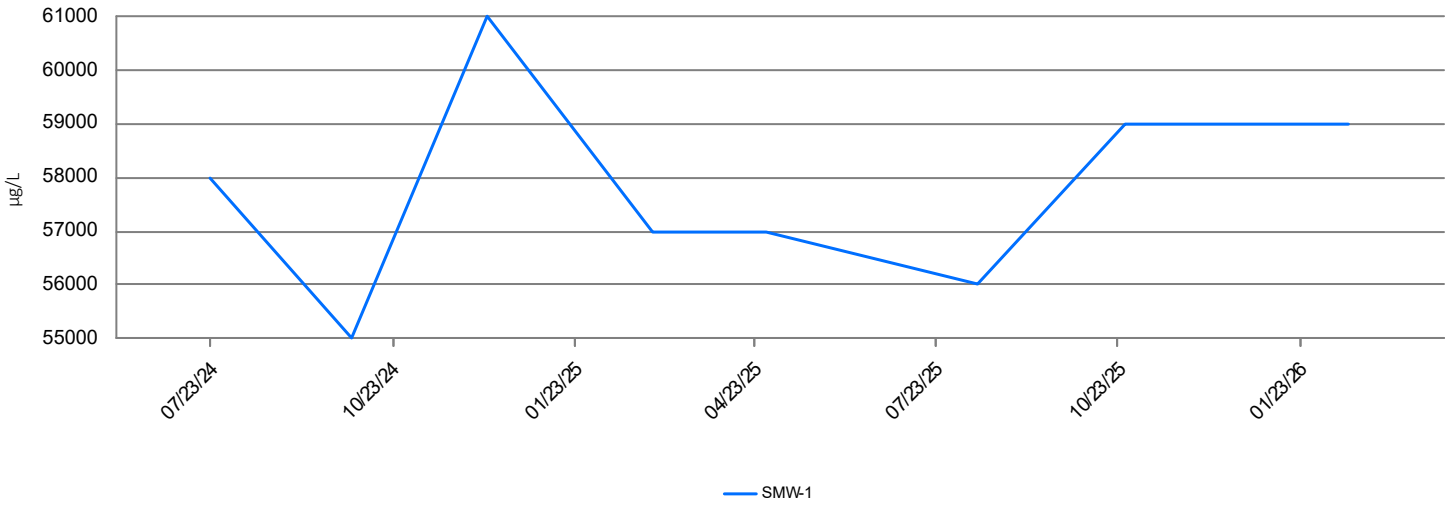
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

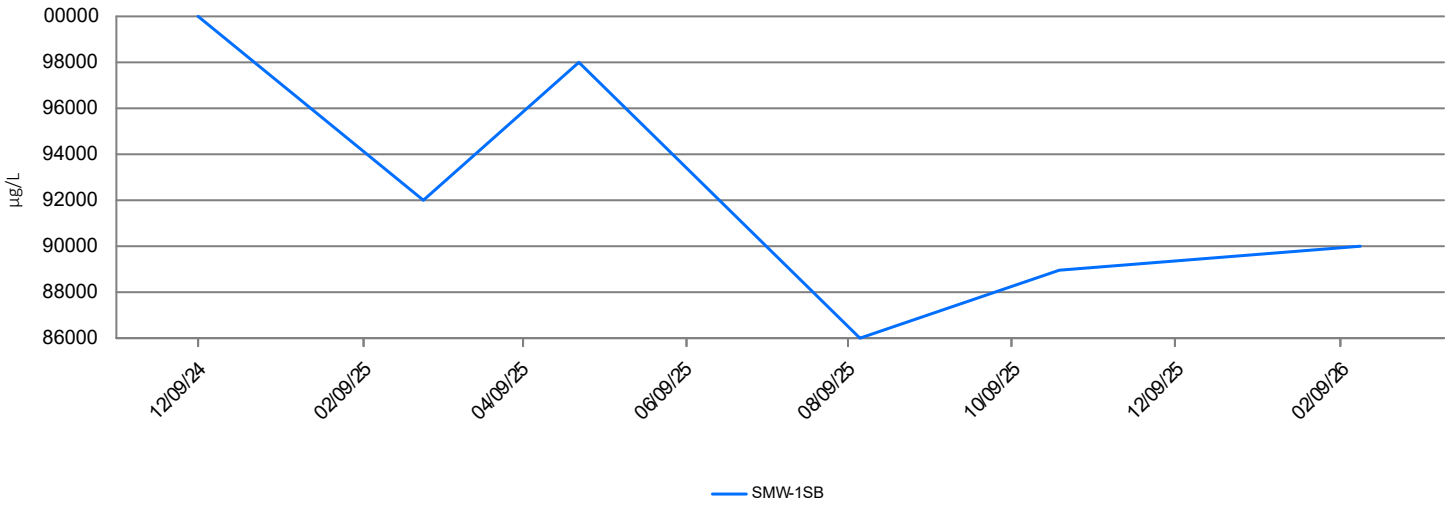
MonitorPro

No Group Selected, Sodium, Total Recoverable (µg/L)

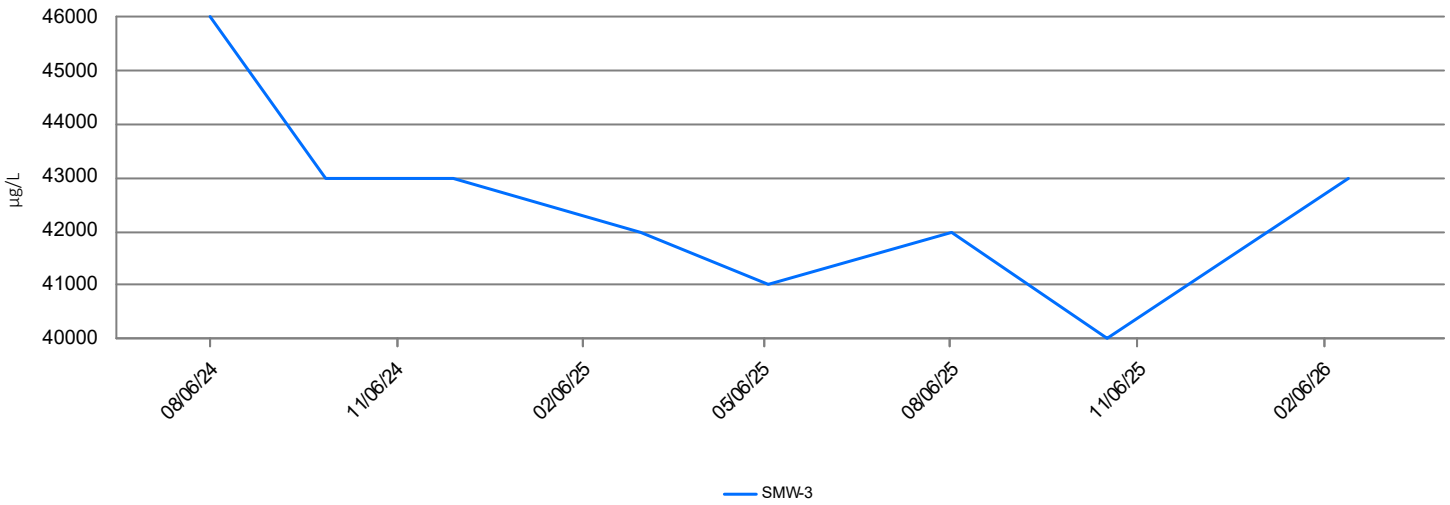
SMW-1



SMW-1SB



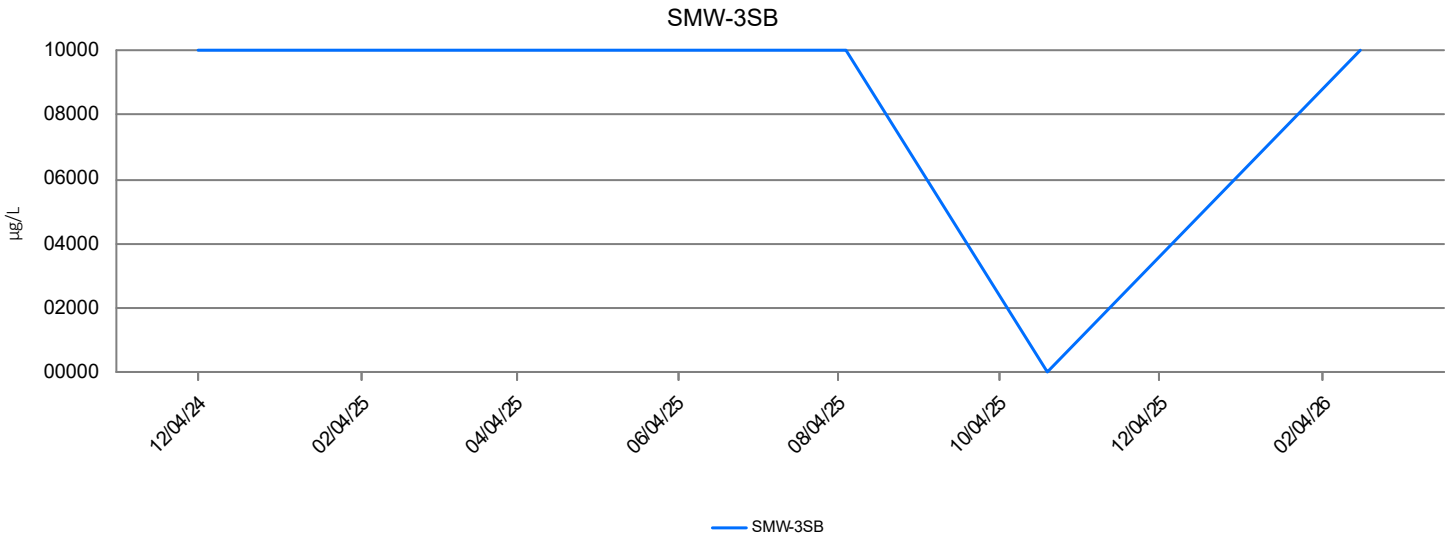
SMW-3



Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

No Group Selected, Sodium, Total Recoverable (µg/L)

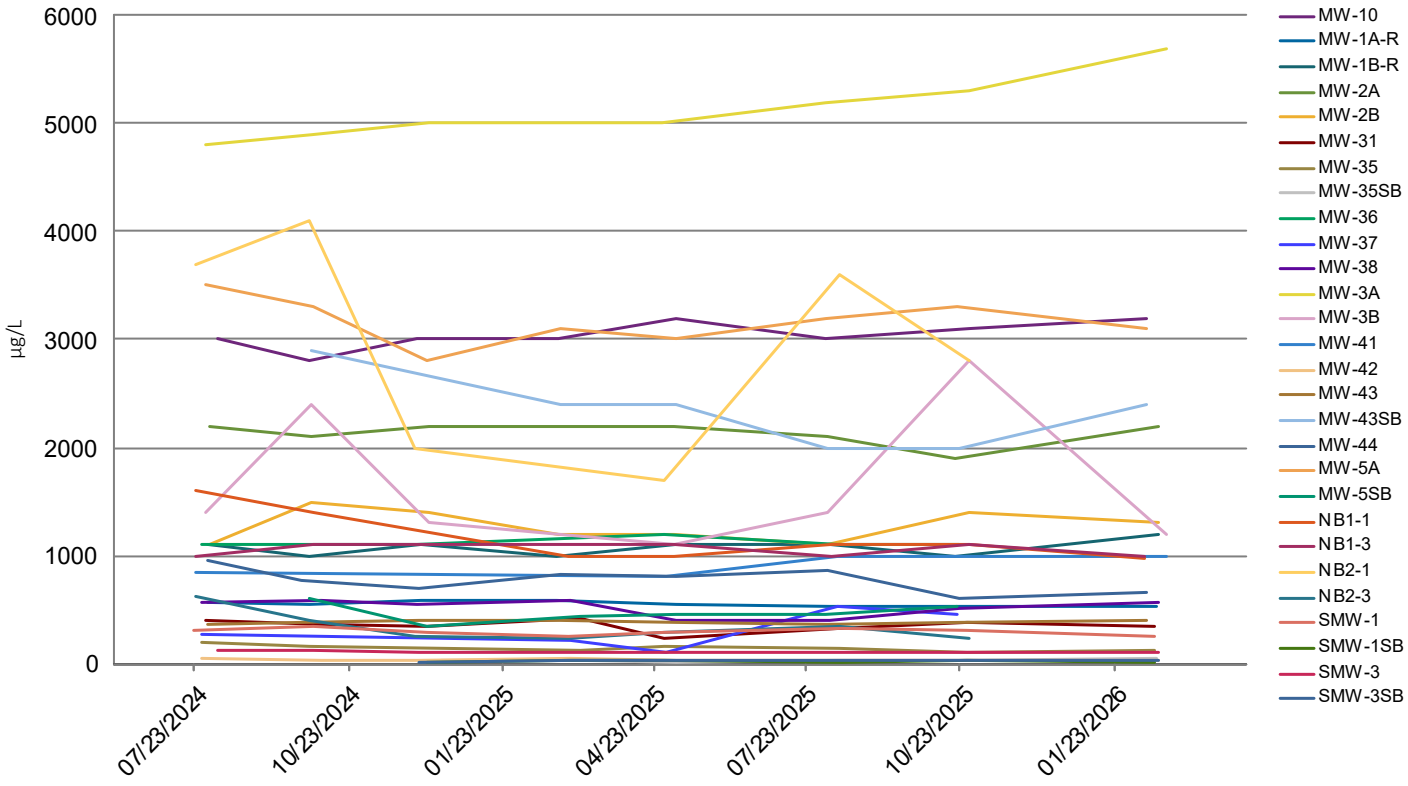


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Strontium, Dissolved (µg/L)

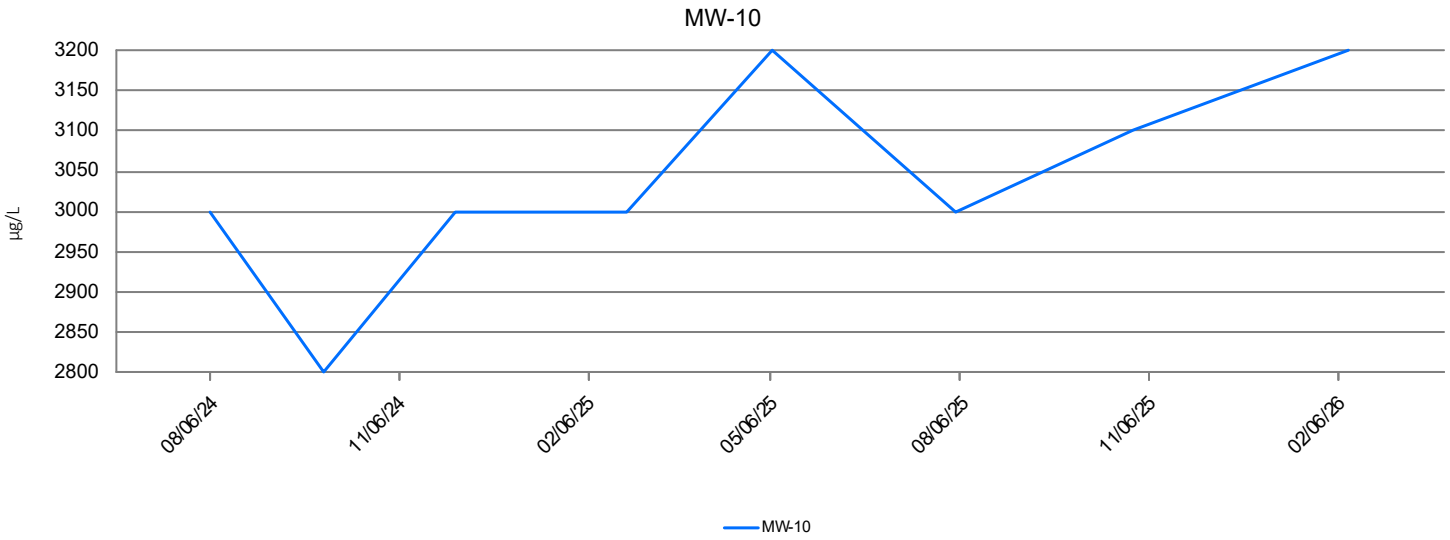


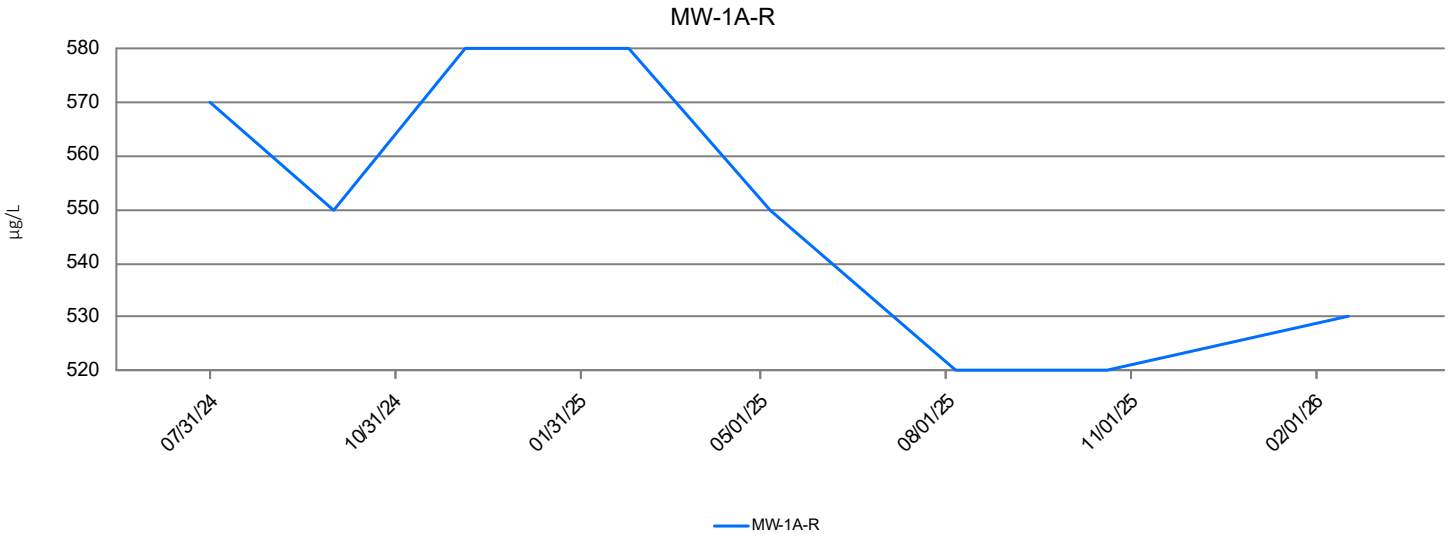
Variable Graphical Report

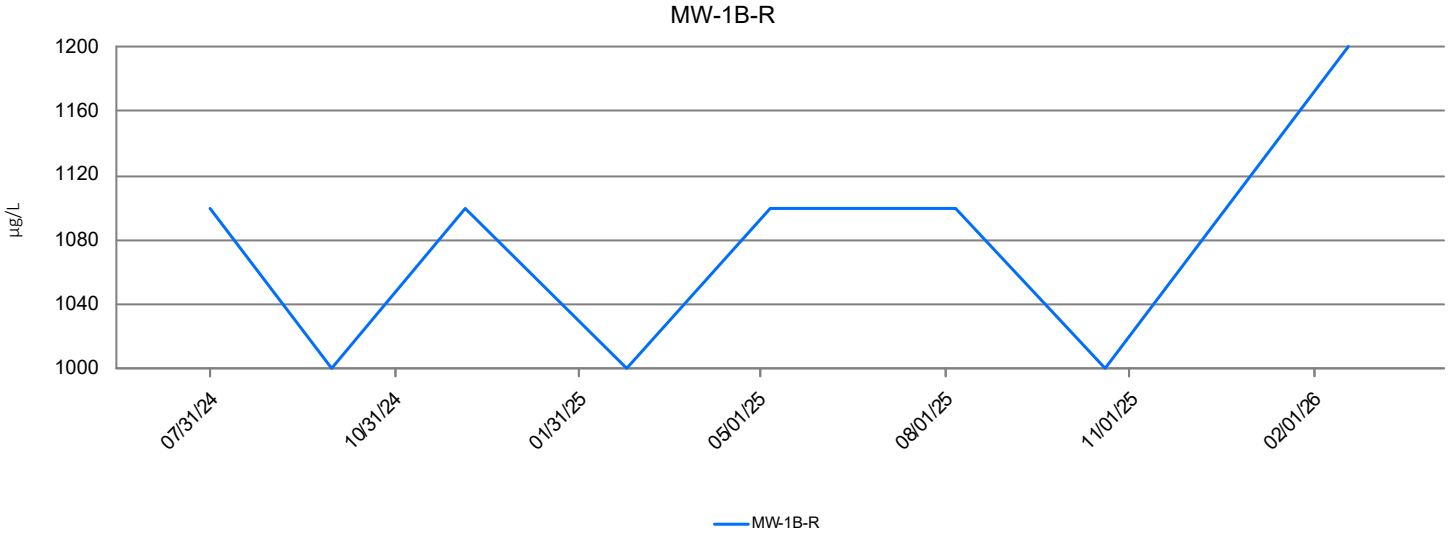
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Strontium, Dissolved (µg/L)







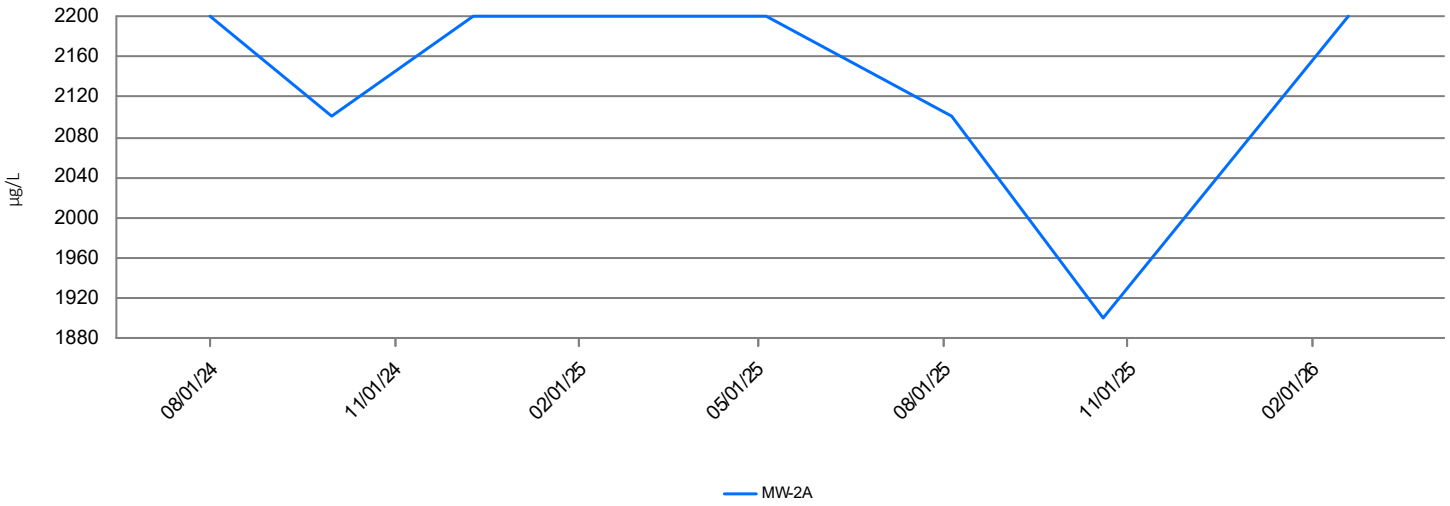
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

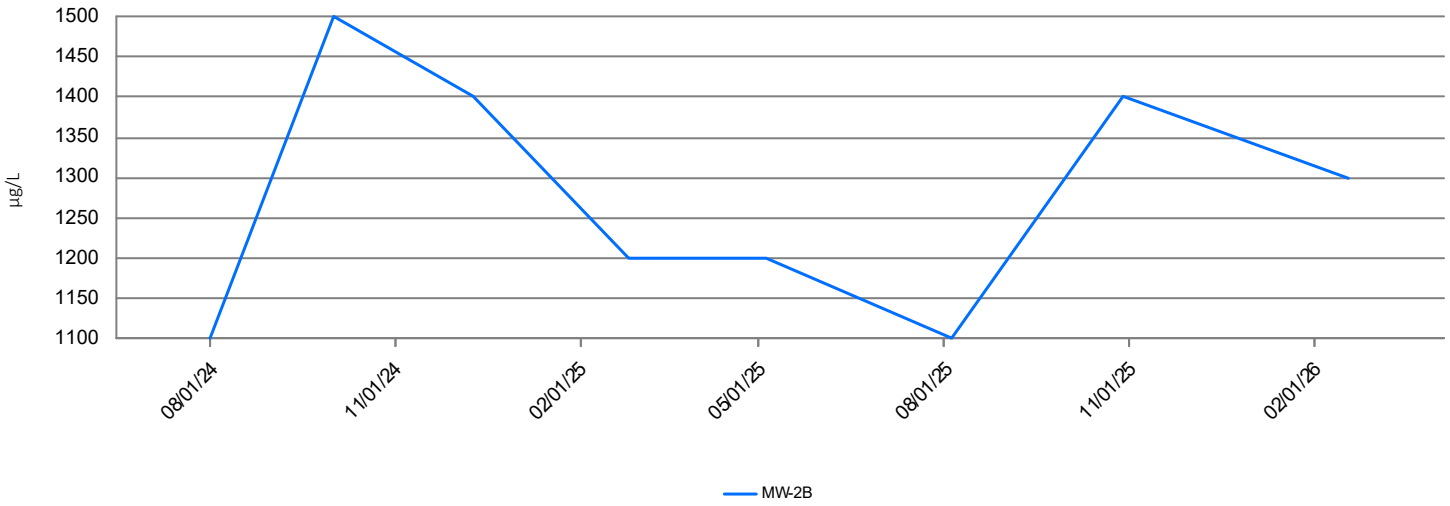
MonitorPro

No Group Selected, Strontium, Dissolved (µg/L)

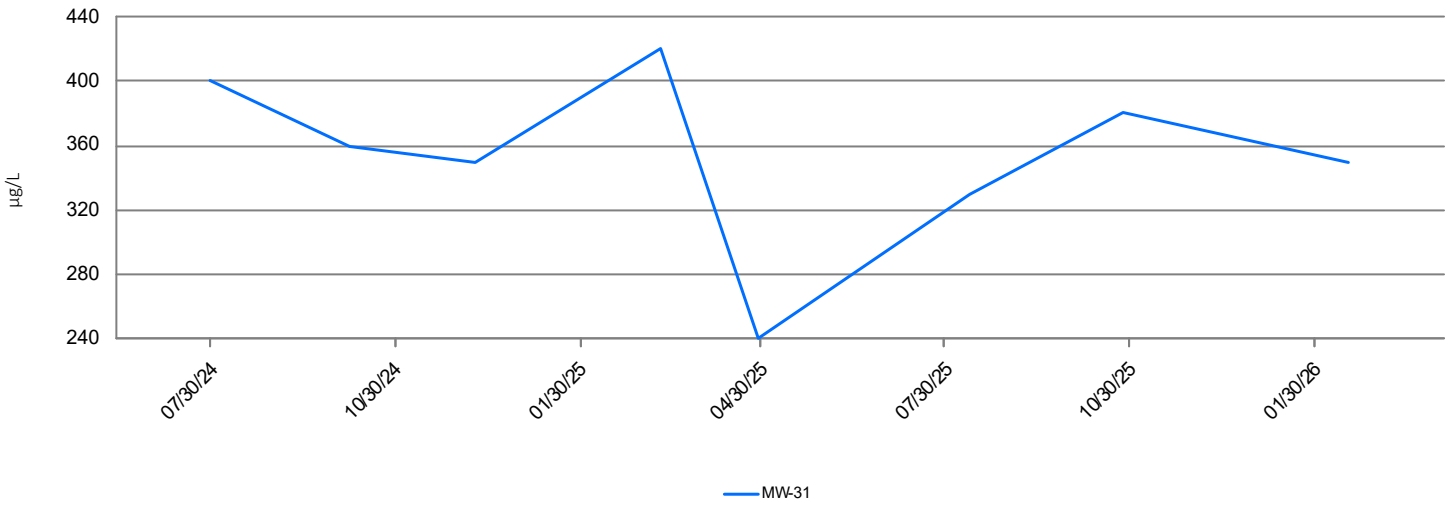
MW-2A



MW-2B



MW-31



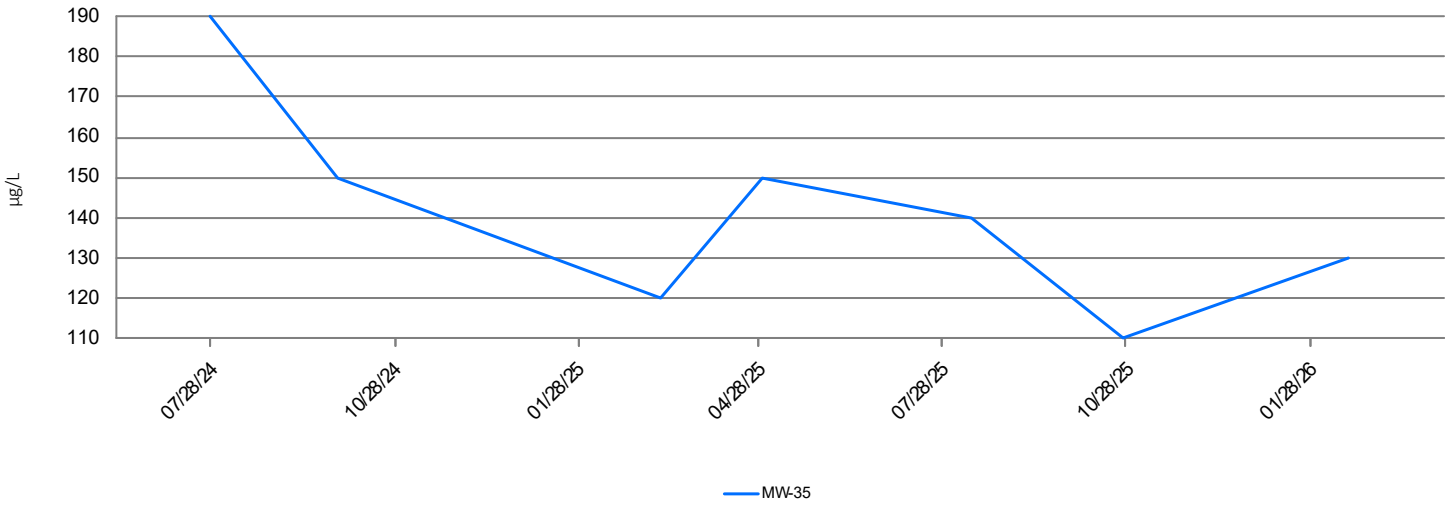
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

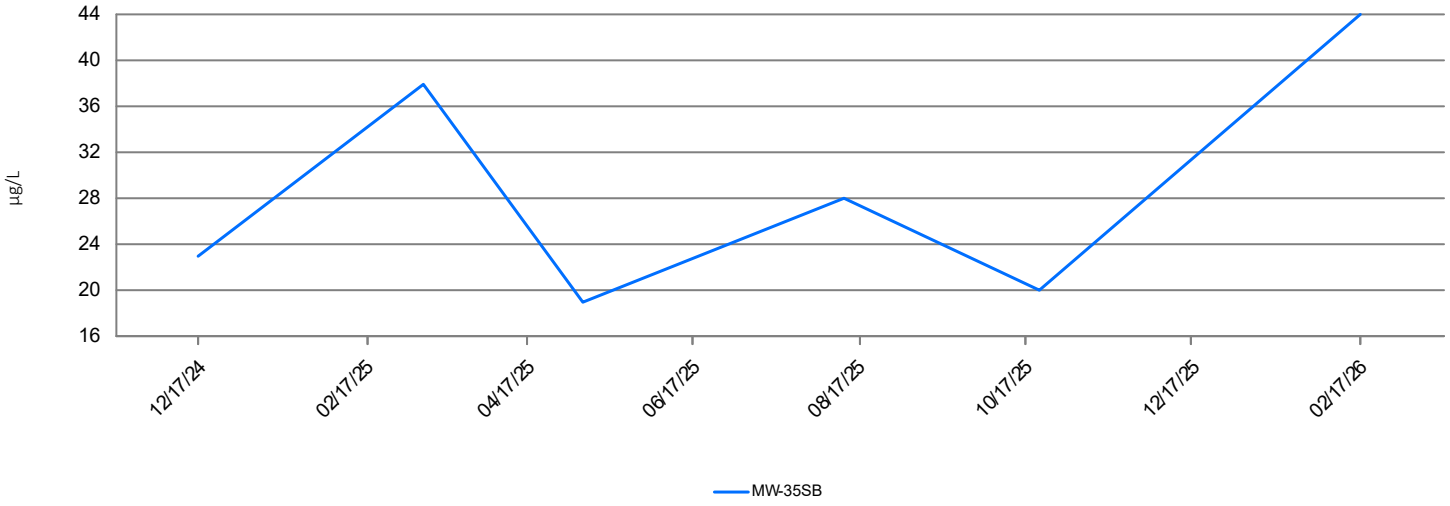
MonitorPro

No Group Selected, Strontium, Dissolved (µg/L)

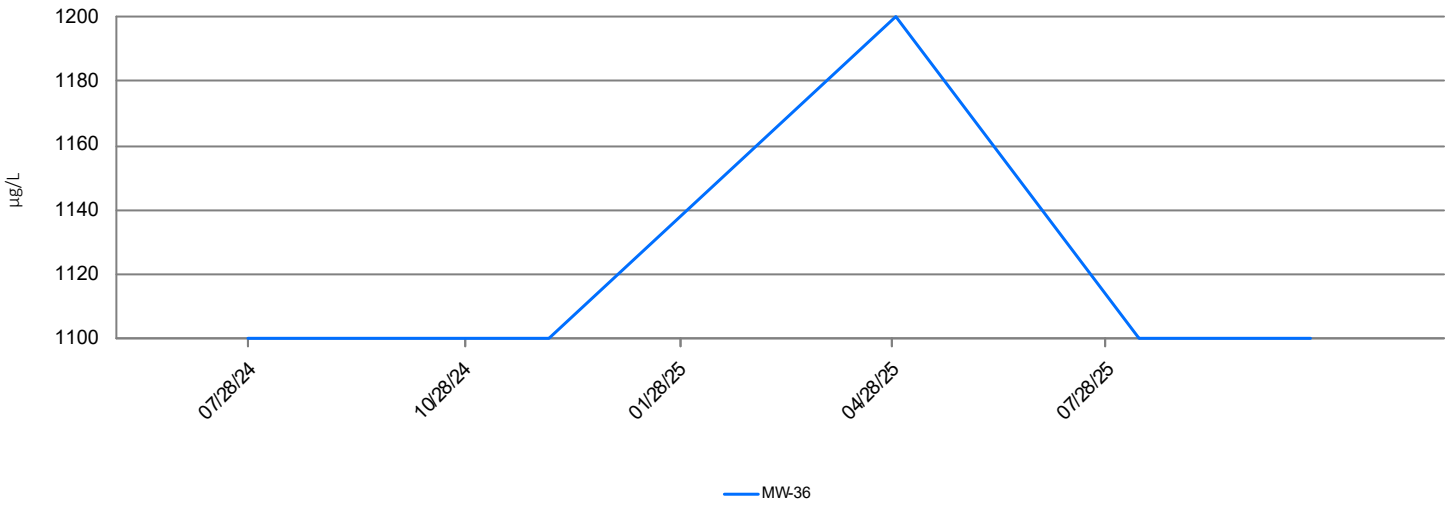
MW-35



MW-35SB



MW-36



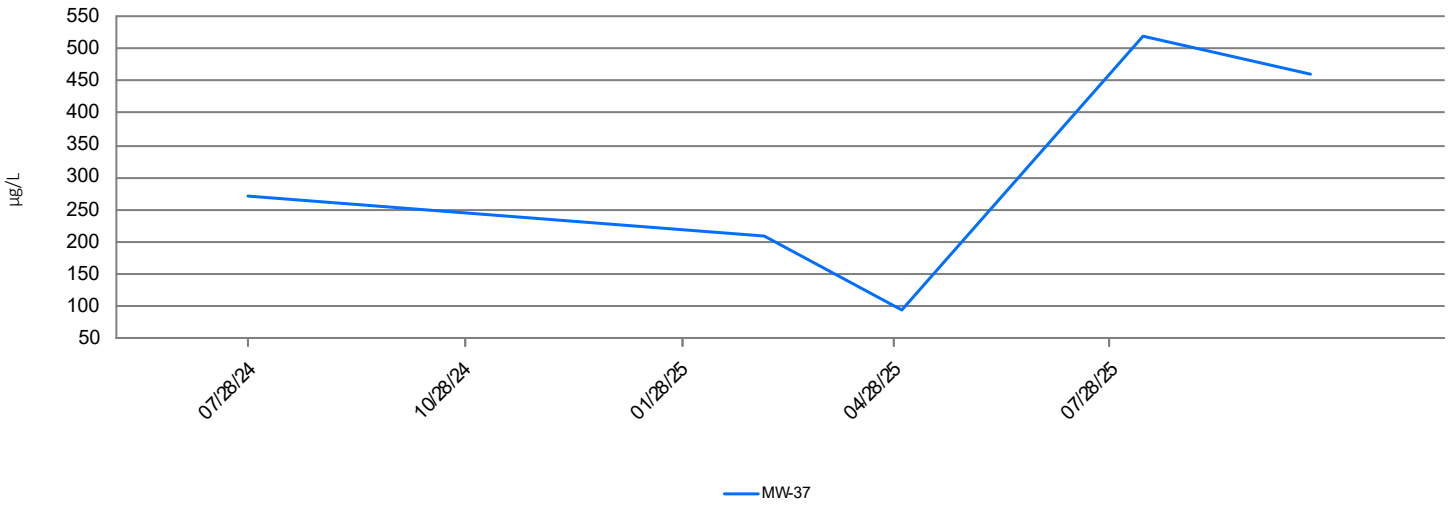
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

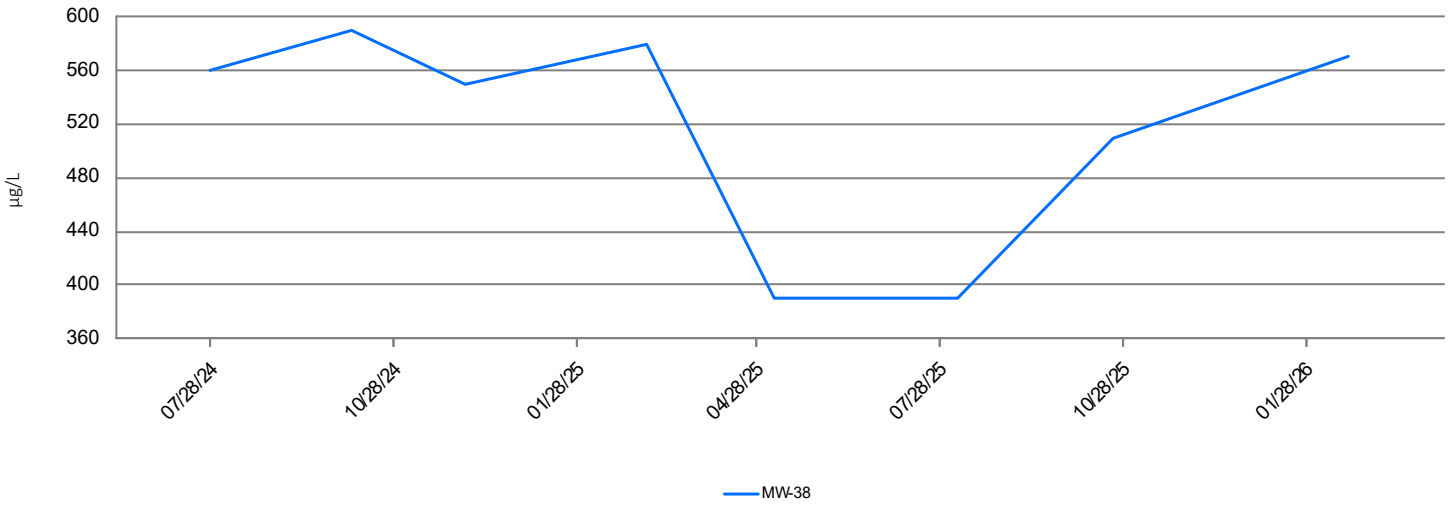
MonitorPro

No Group Selected, Strontium, Dissolved (µg/L)

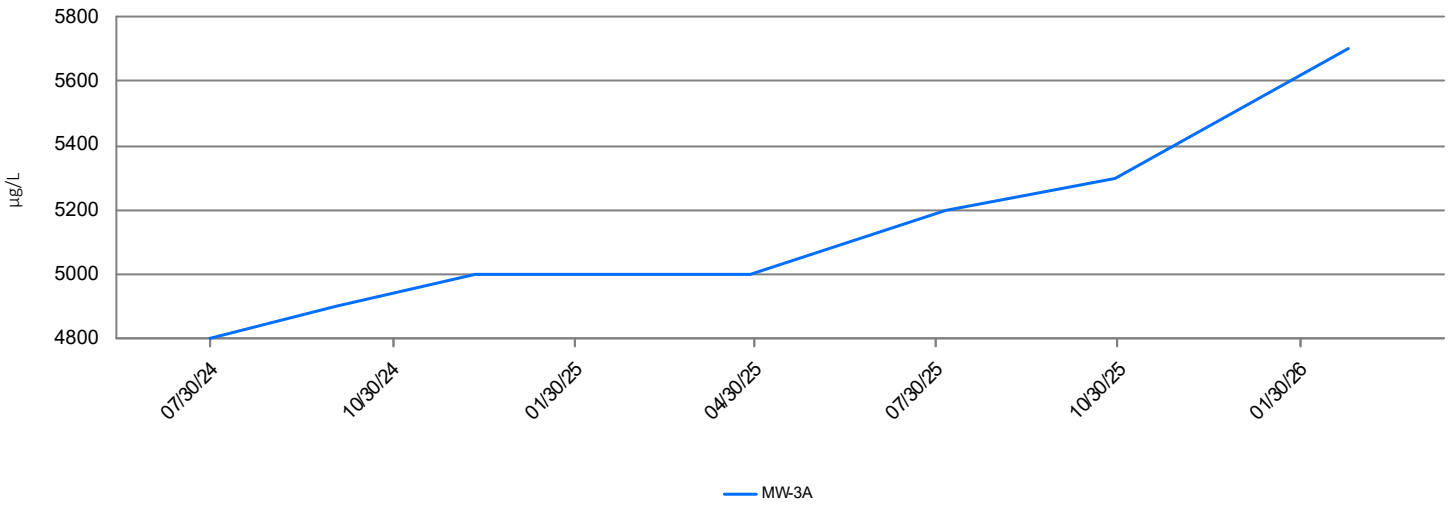
MW-37



MW-38



MW-3A



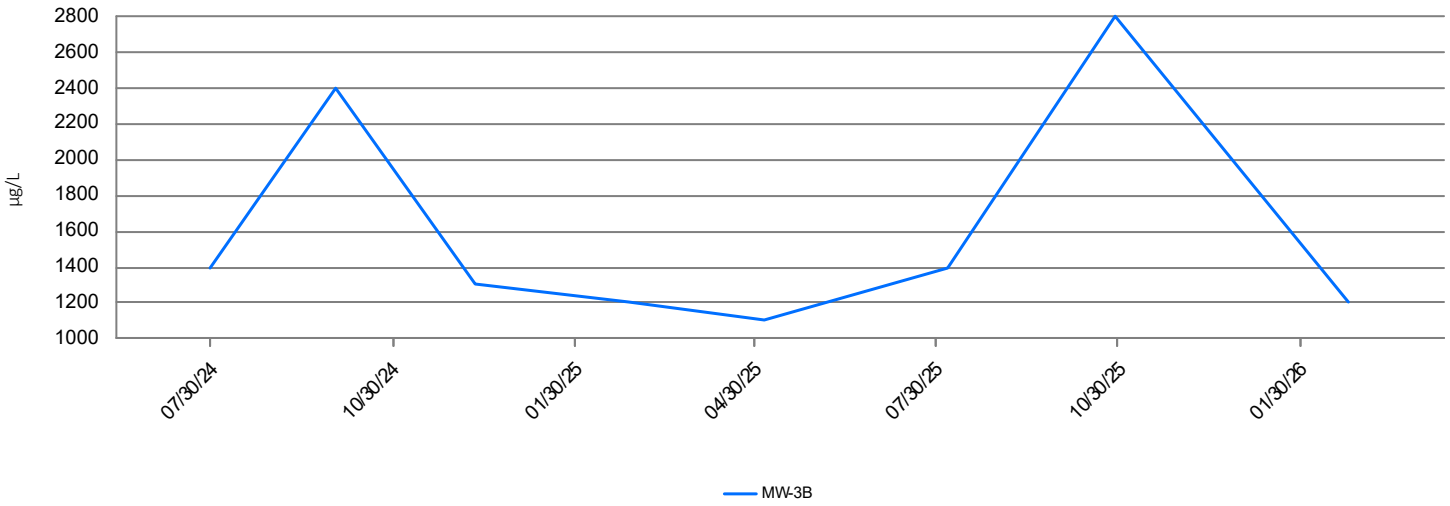
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

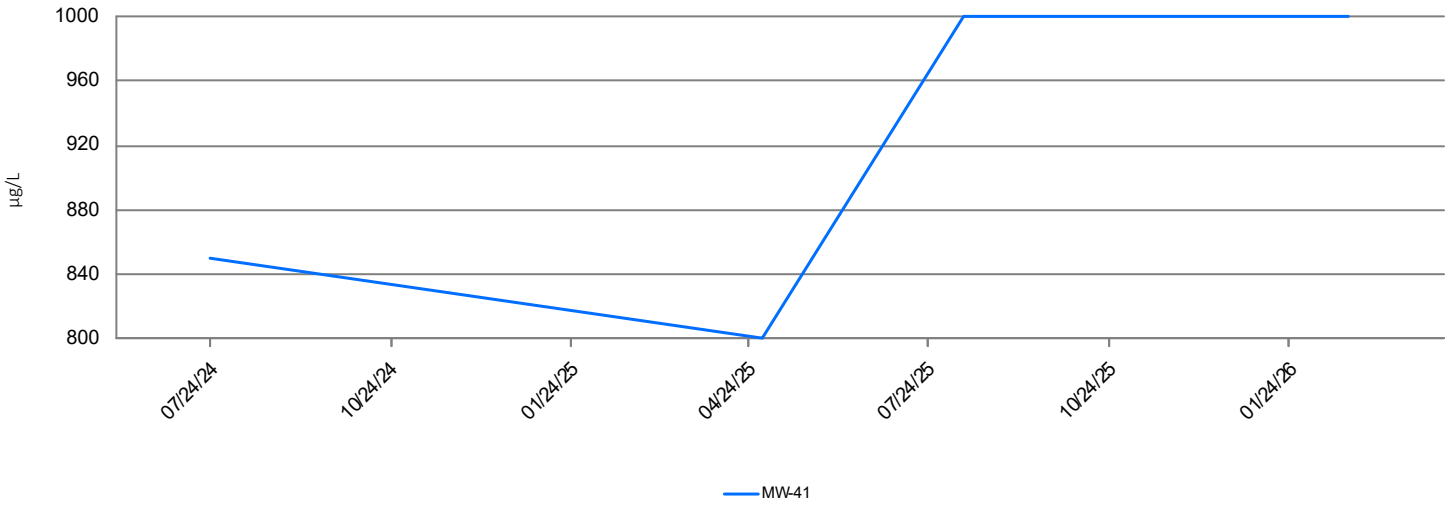
MonitorPro

No Group Selected, Strontium, Dissolved (µg/L)

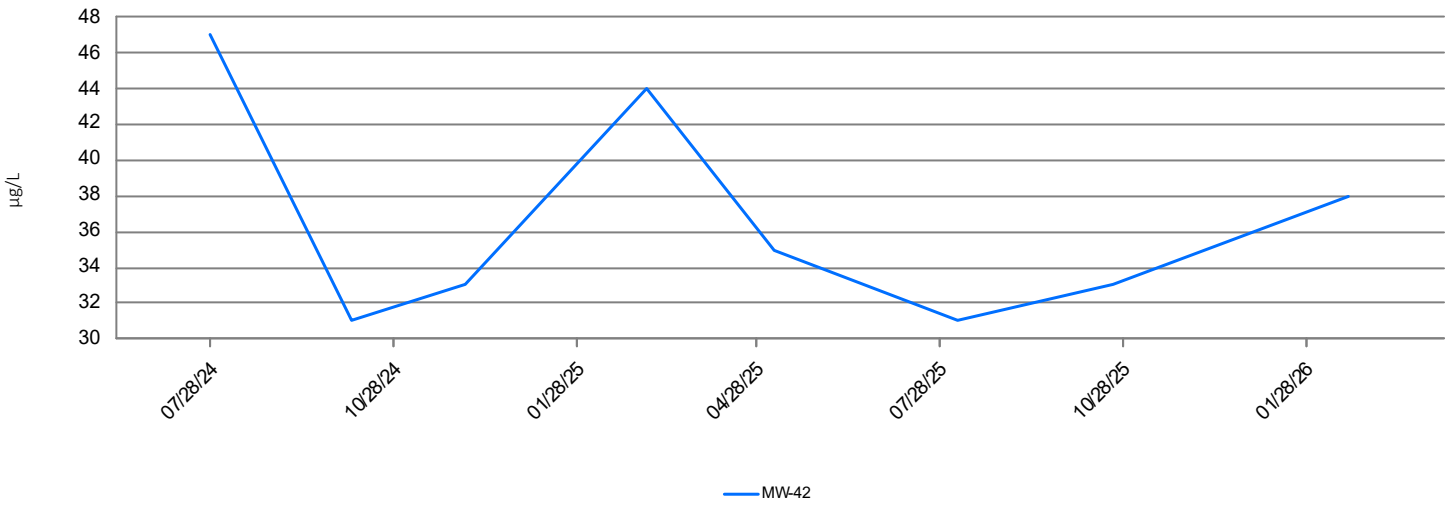
MW-3B



MW-41



MW-42



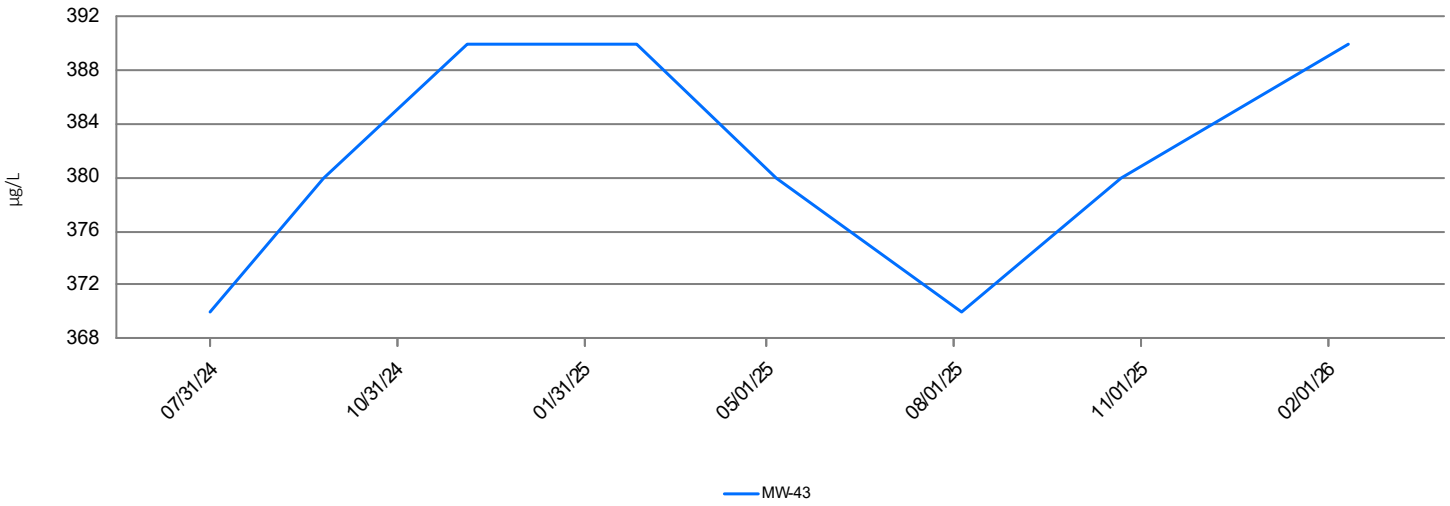
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

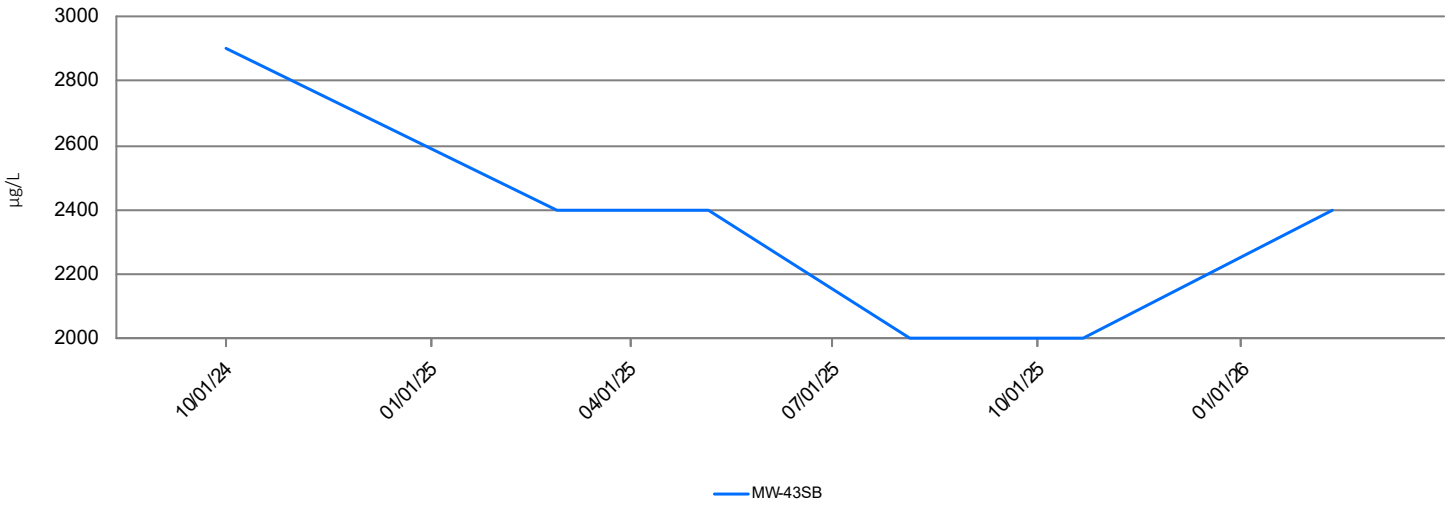
MonitorPro

No Group Selected, Strontium, Dissolved (µg/L)

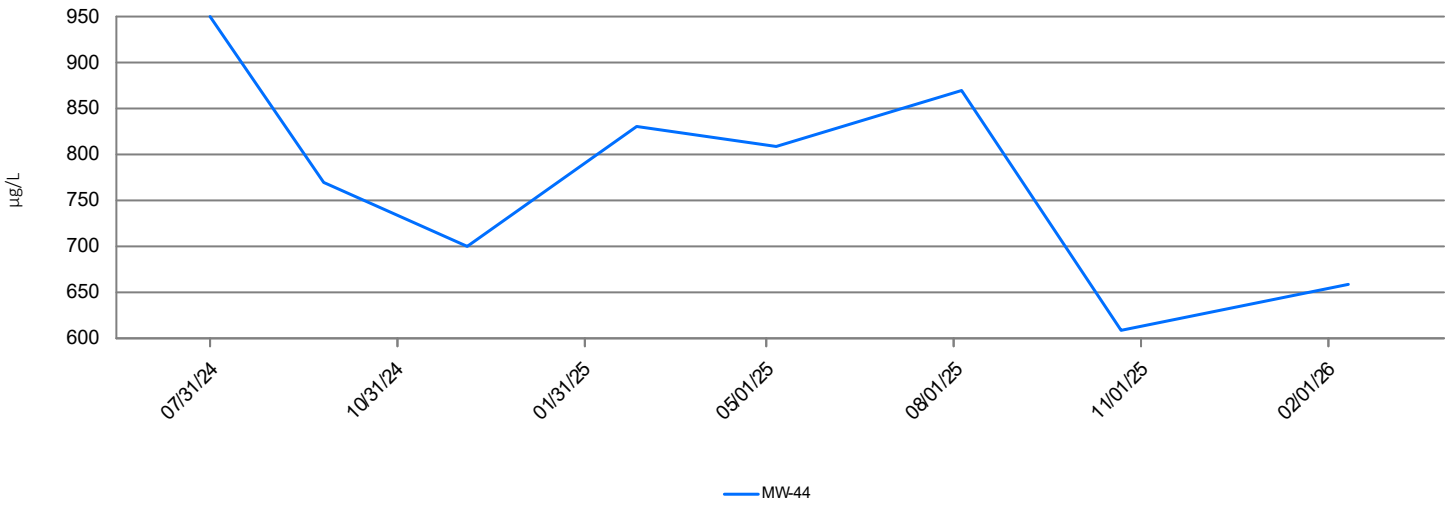
MW-43



MW-43SB



MW-44



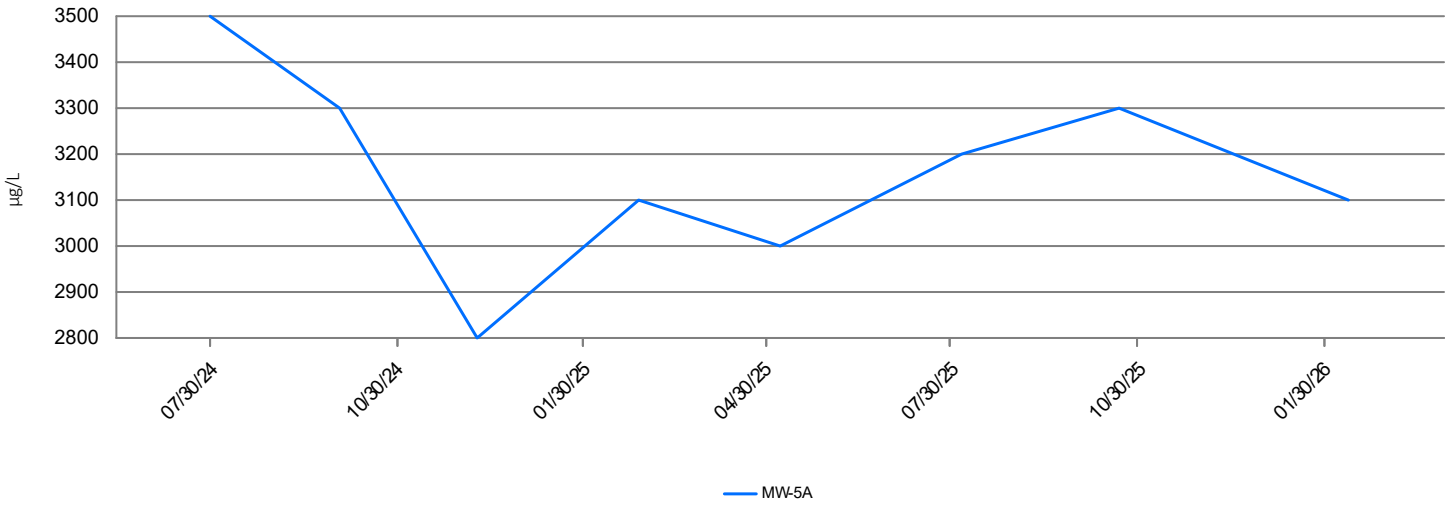
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

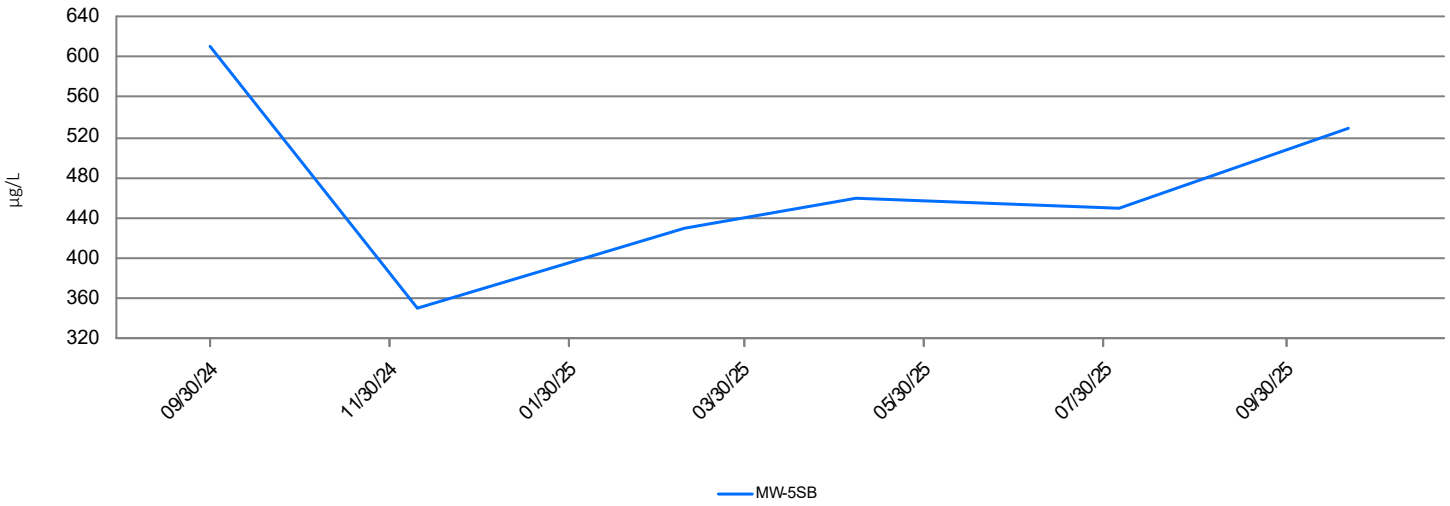
MonitorPro

No Group Selected, Strontium, Dissolved (µg/L)

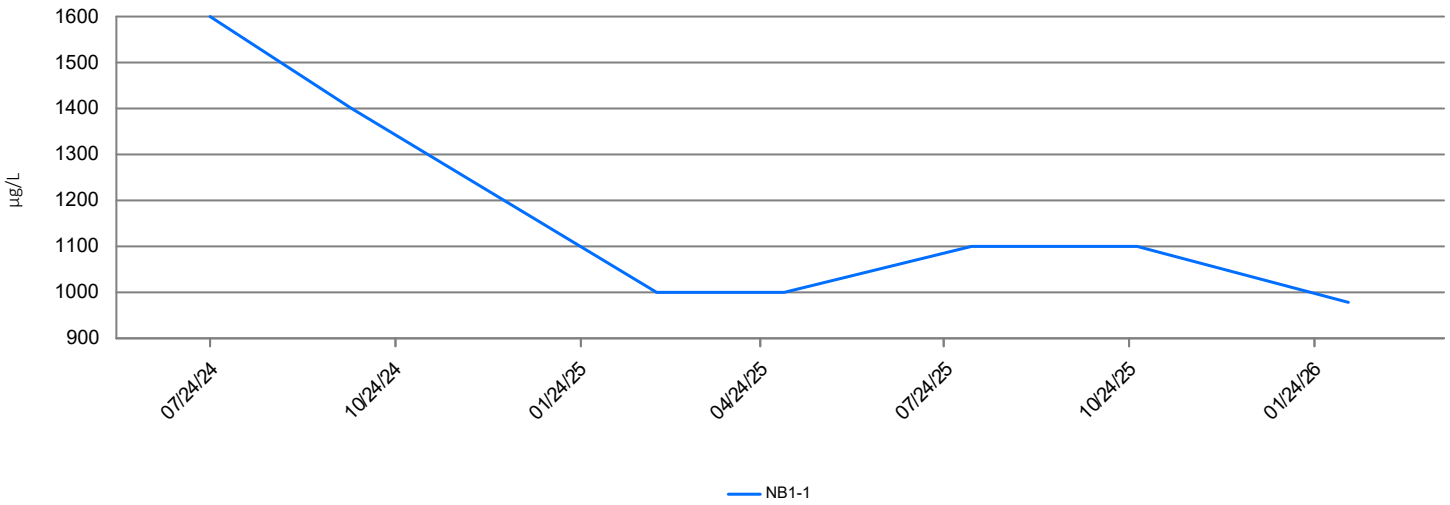
MW-5A



MW-5SB



NB1-1

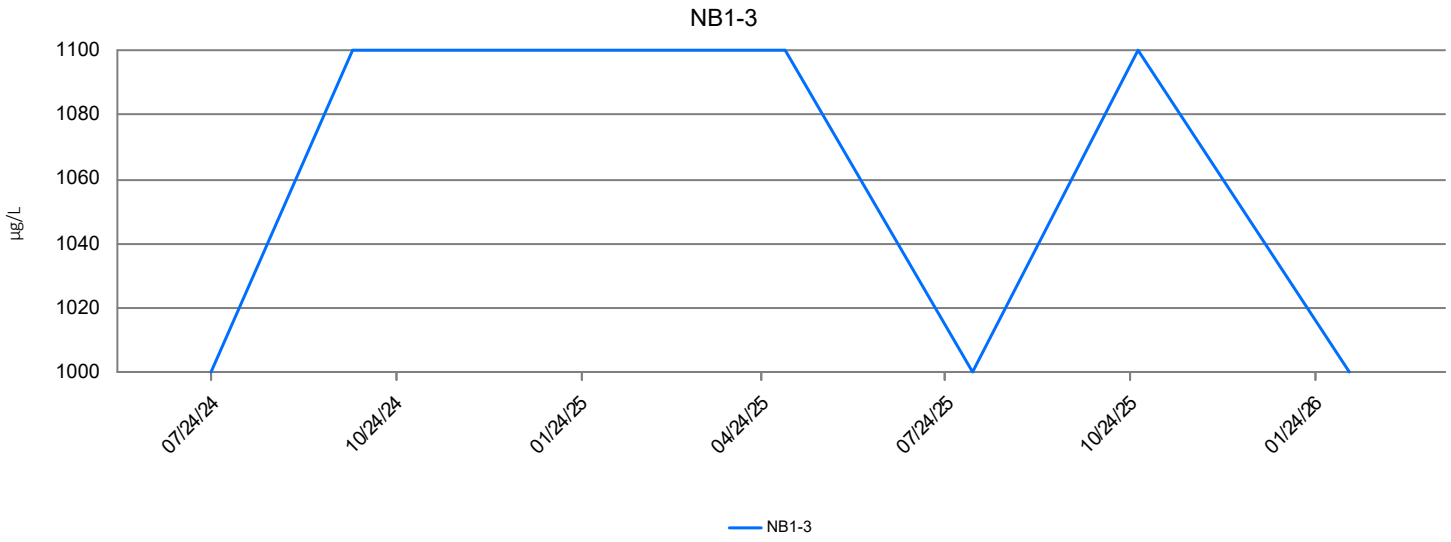


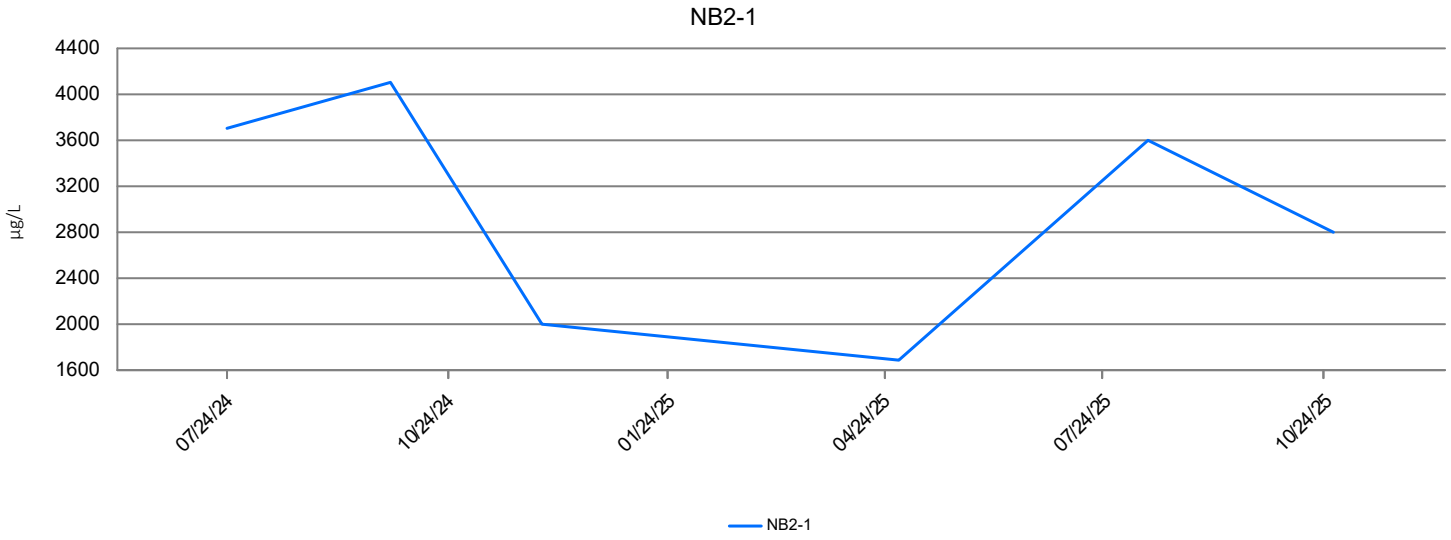
Variable Graphical Report

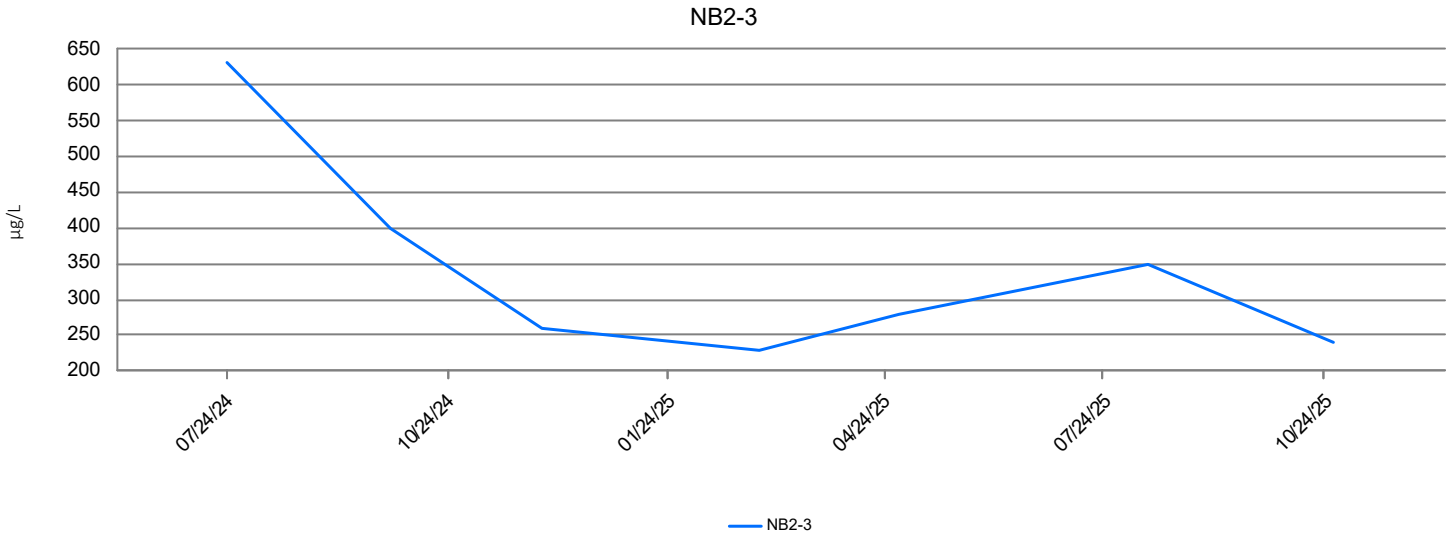
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Strontium, Dissolved (µg/L)







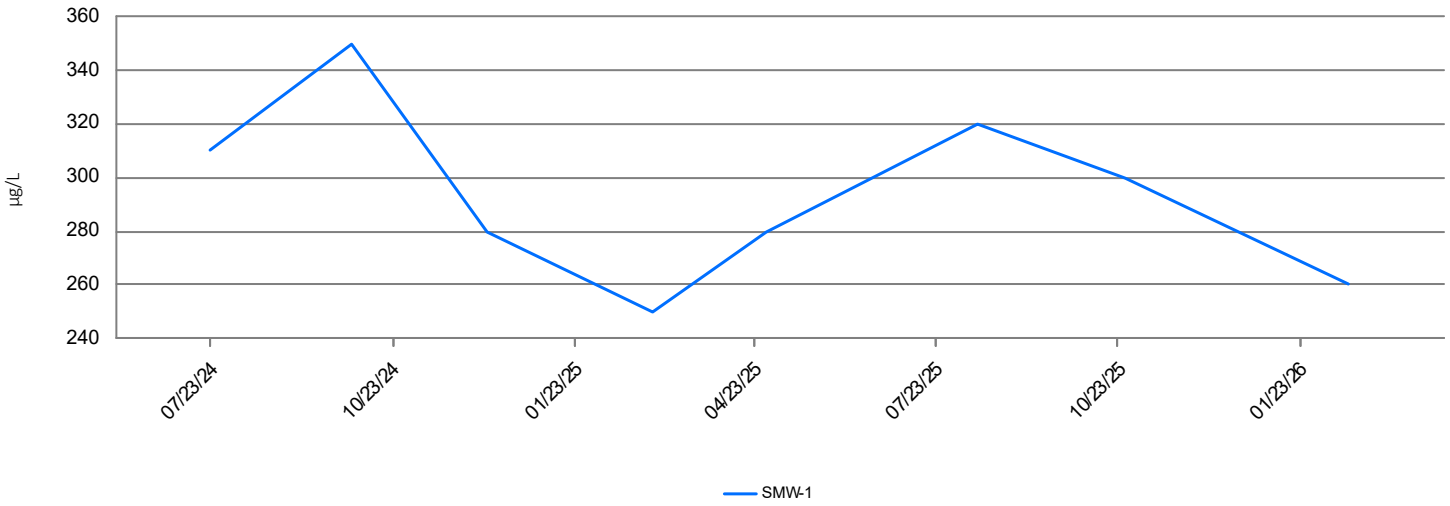
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

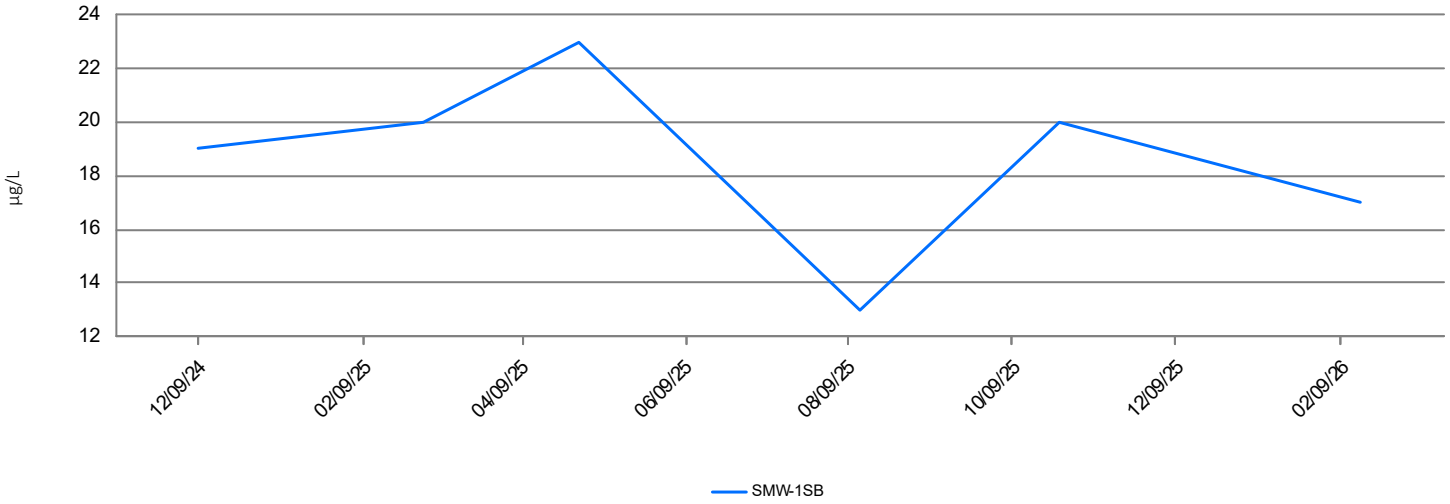
MonitorPro

No Group Selected, Strontium, Dissolved (µg/L)

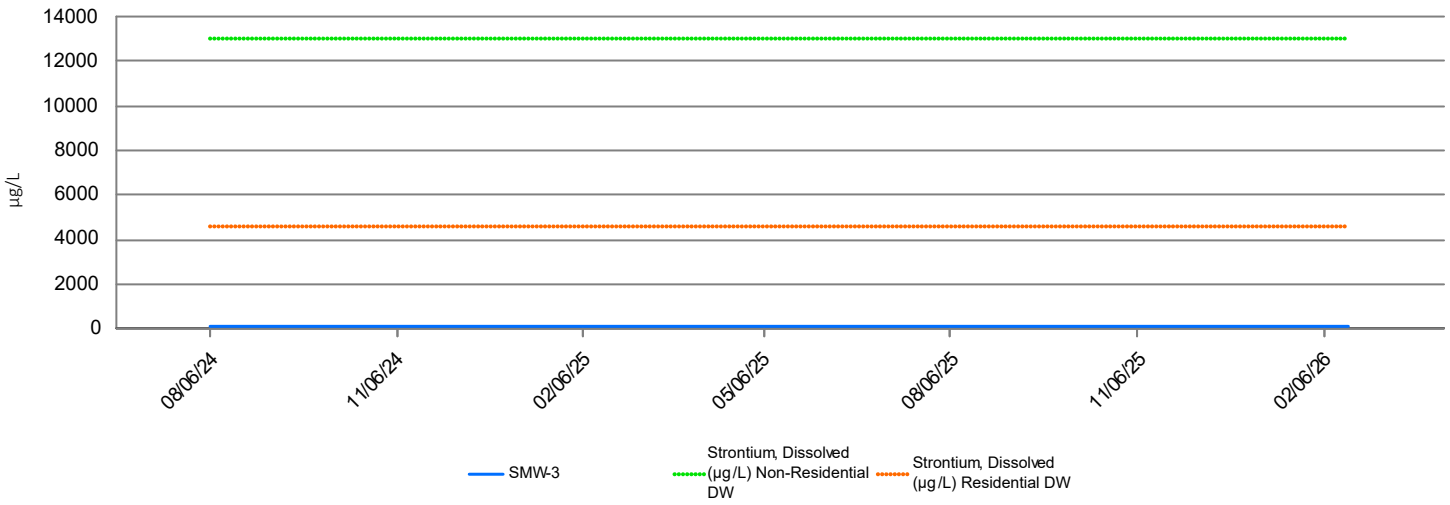
SMW-1



SMW-1SB



SMW-3

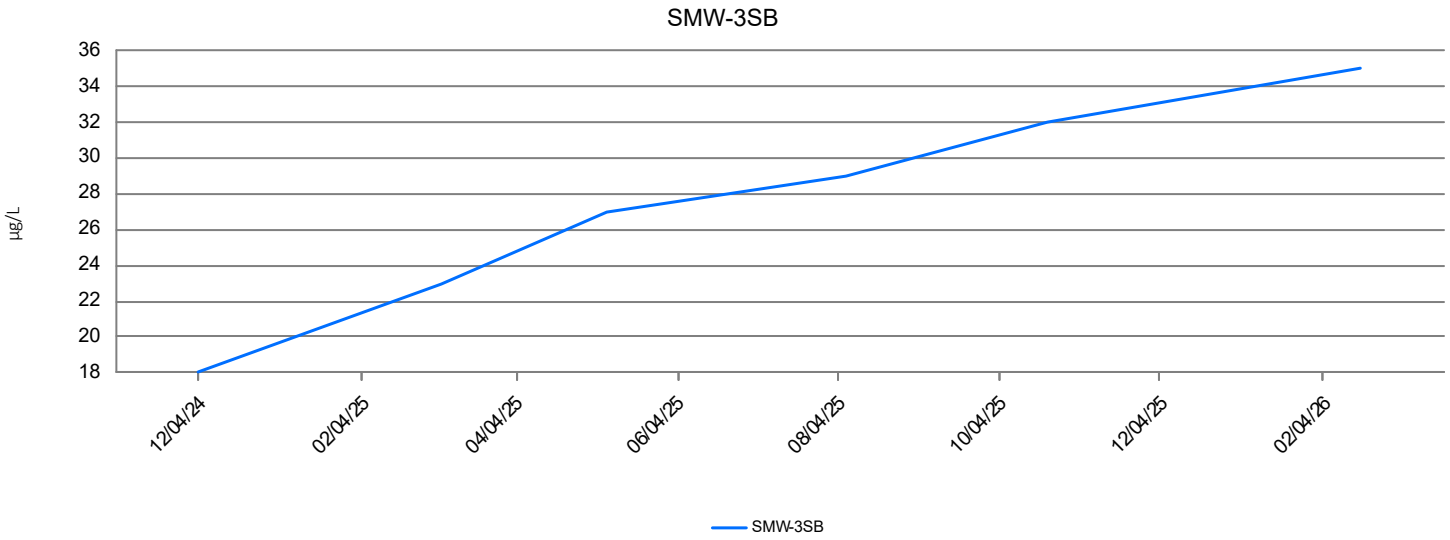


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Strontium, Dissolved (µg/L)

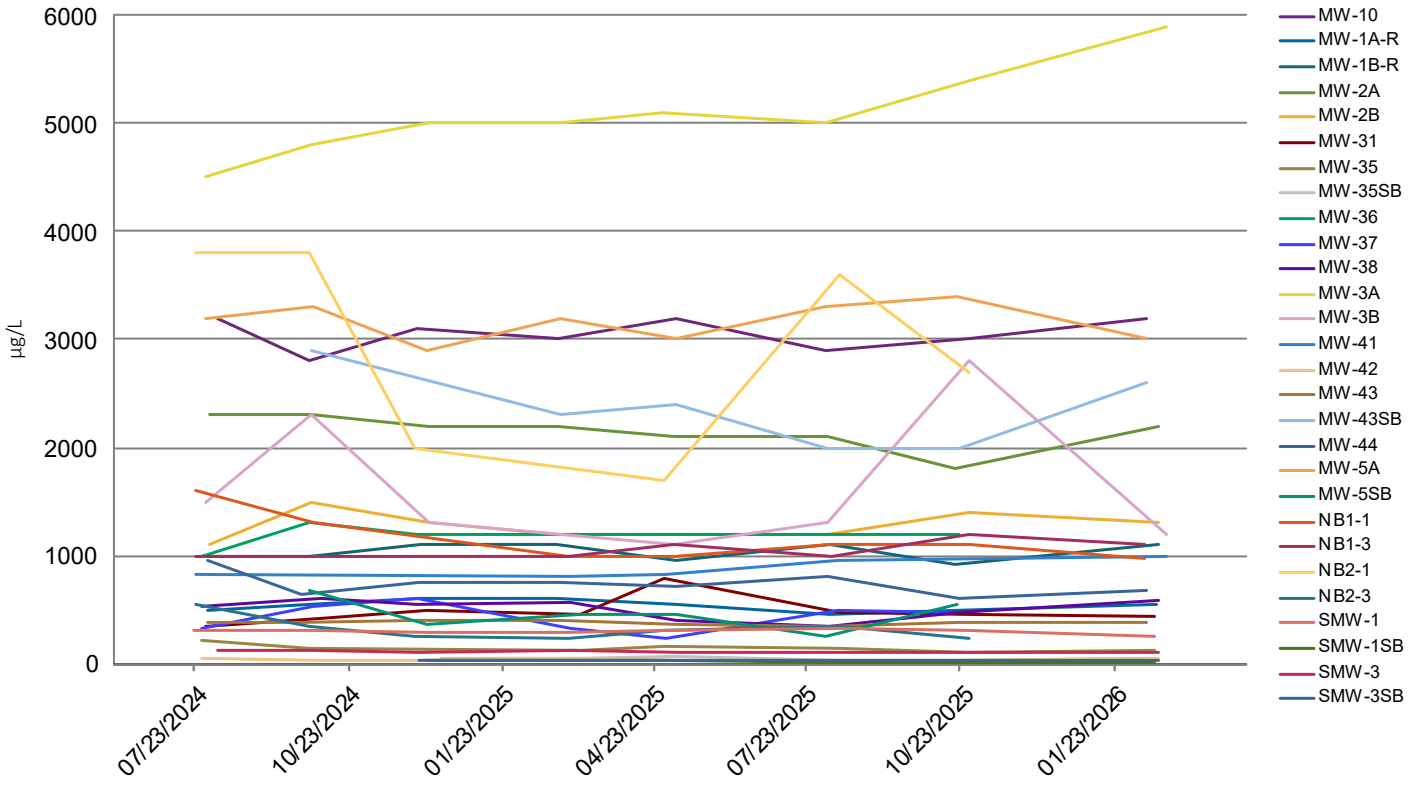


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Strontium, Total Recoverable (µg/L)

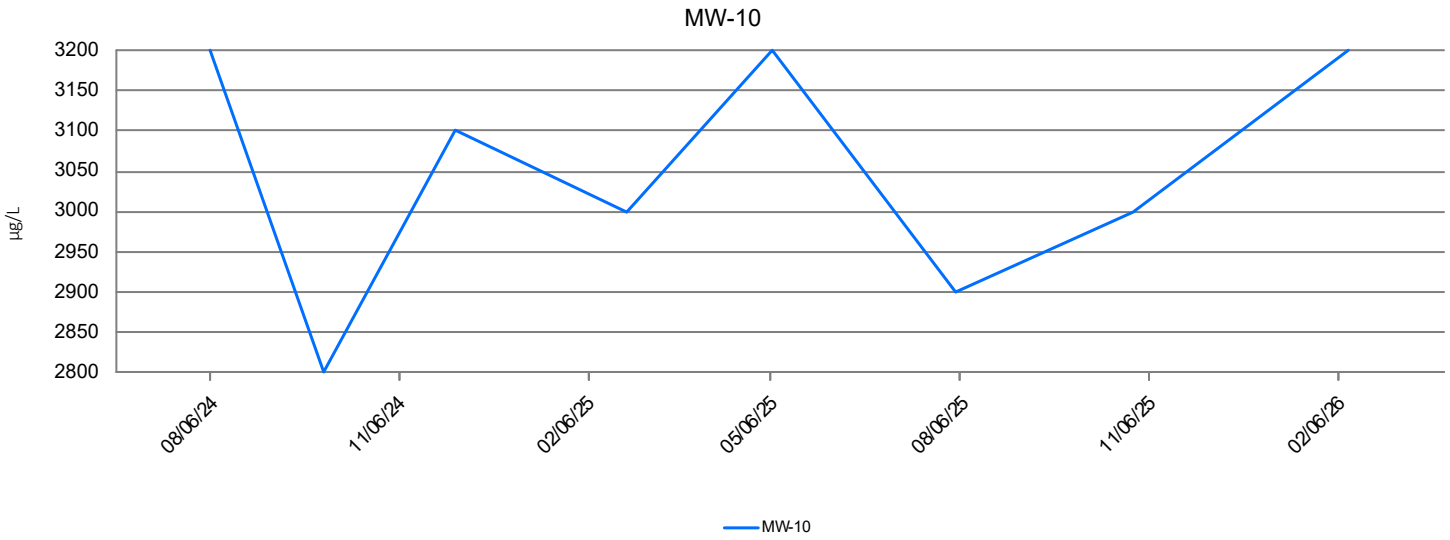


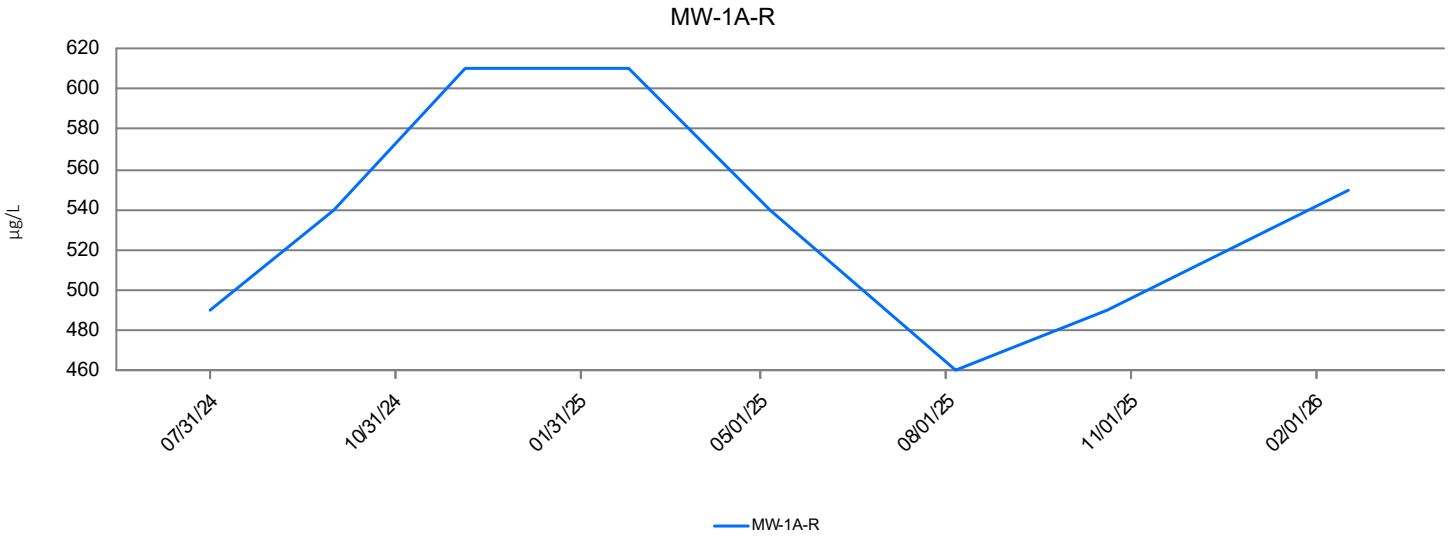
Variable Graphical Report

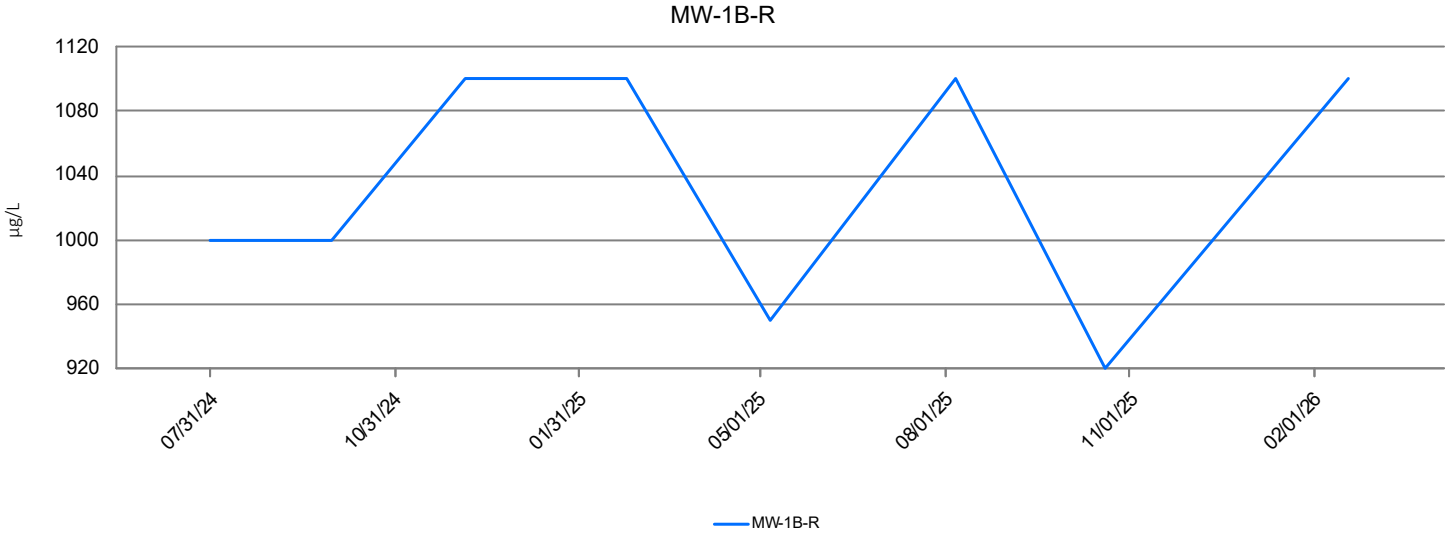
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Strontium, Total Recoverable (µg/L)







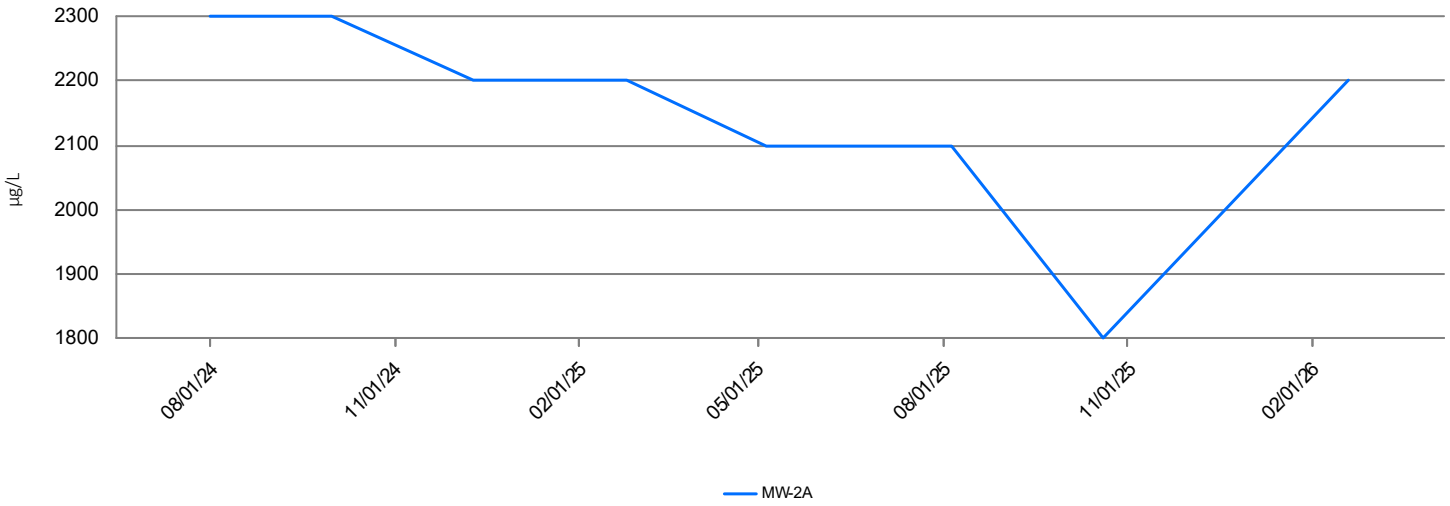
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

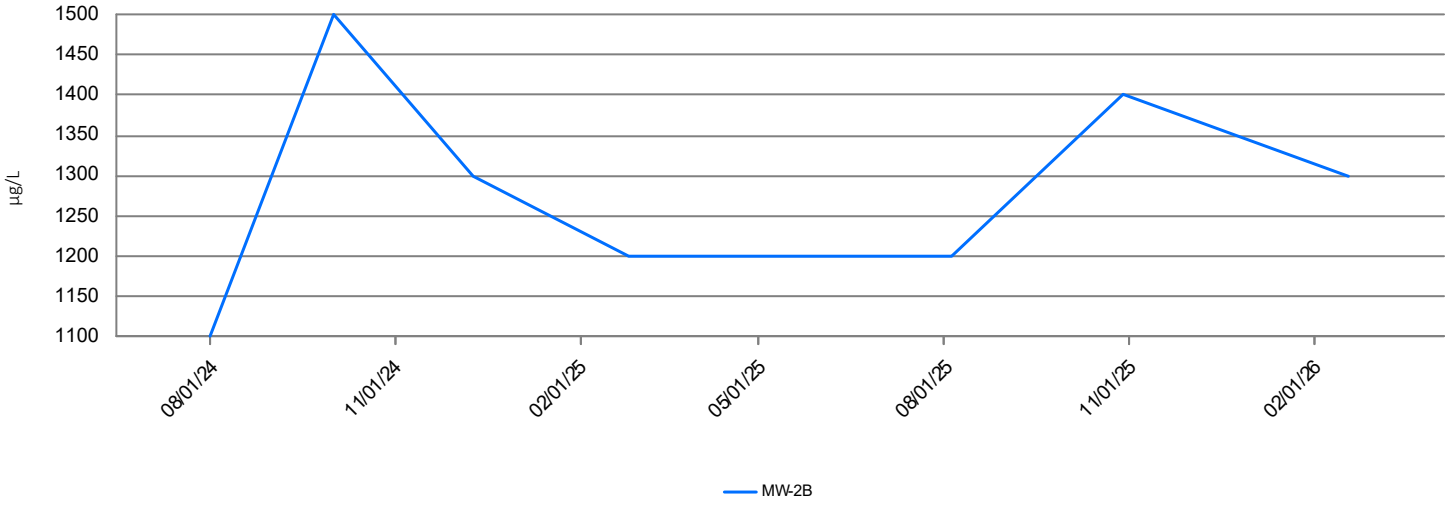
MonitorPro

No Group Selected, Strontium, Total Recoverable (µg/L)

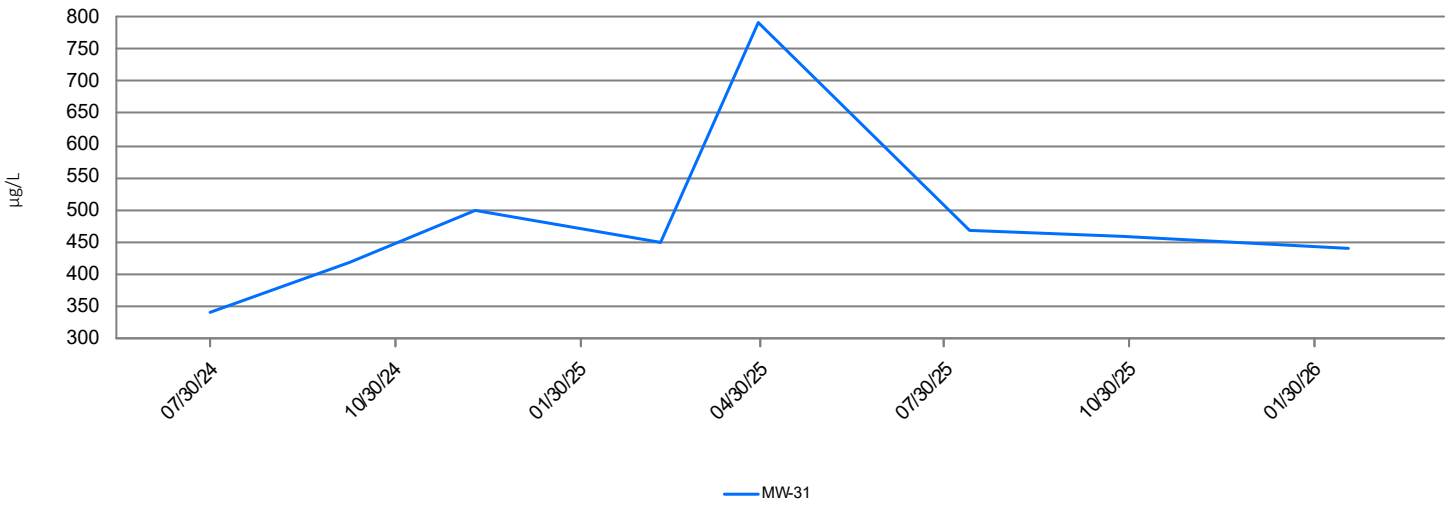
MW-2A



MW-2B



MW-31



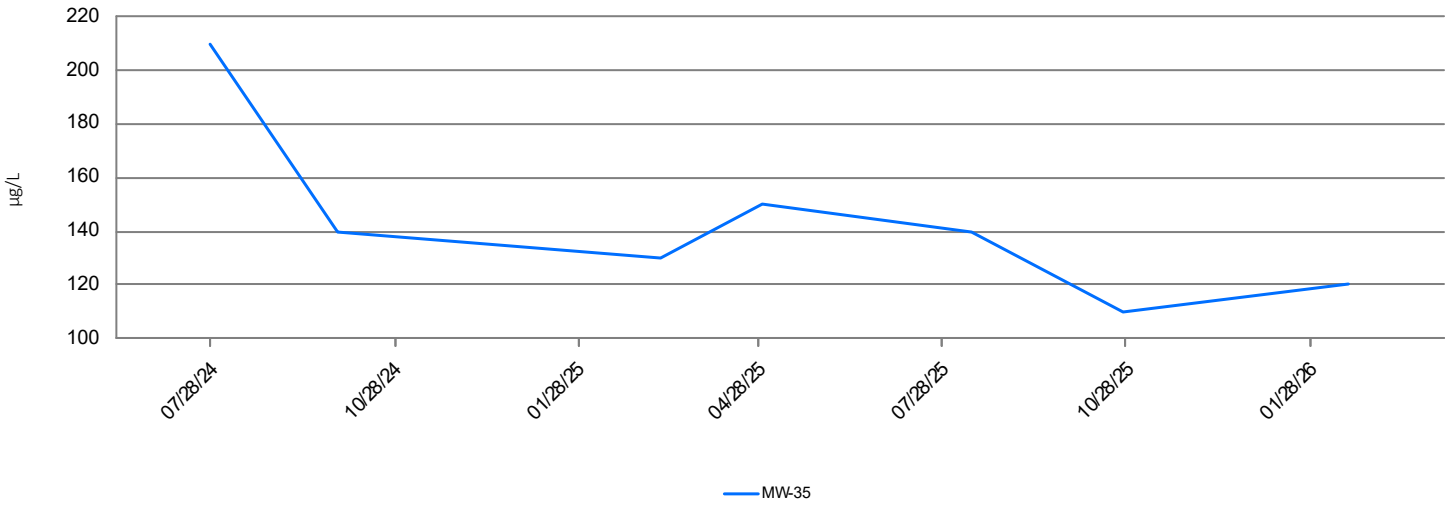
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

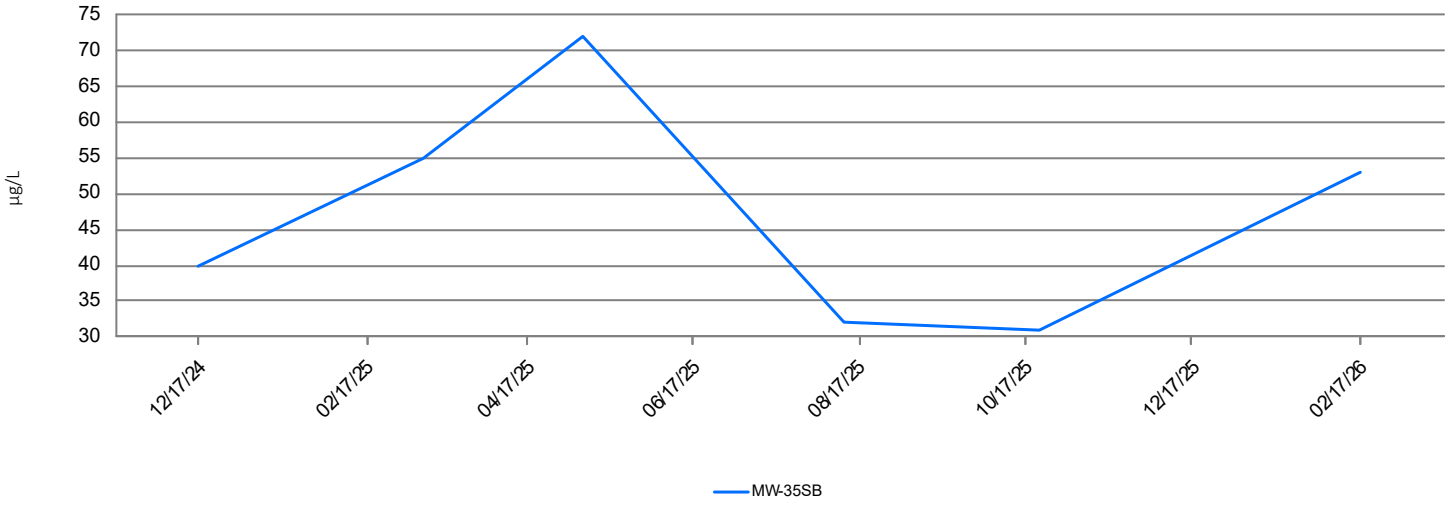
MonitorPro

No Group Selected, Strontium, Total Recoverable (µg/L)

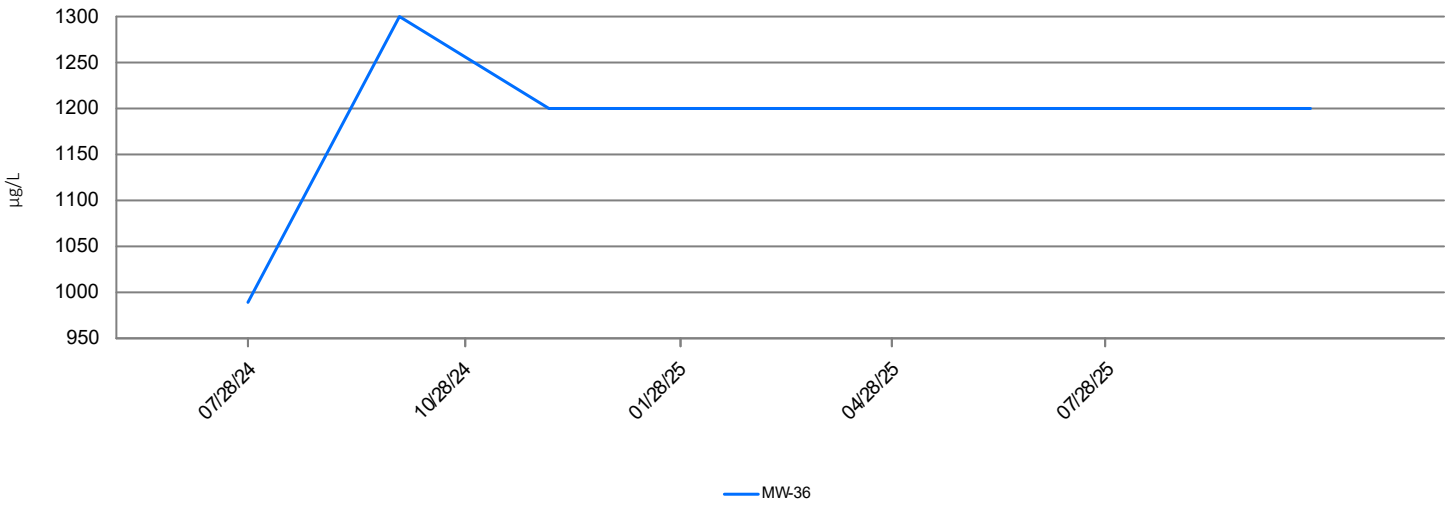
MW-35



MW-35SB



MW-36

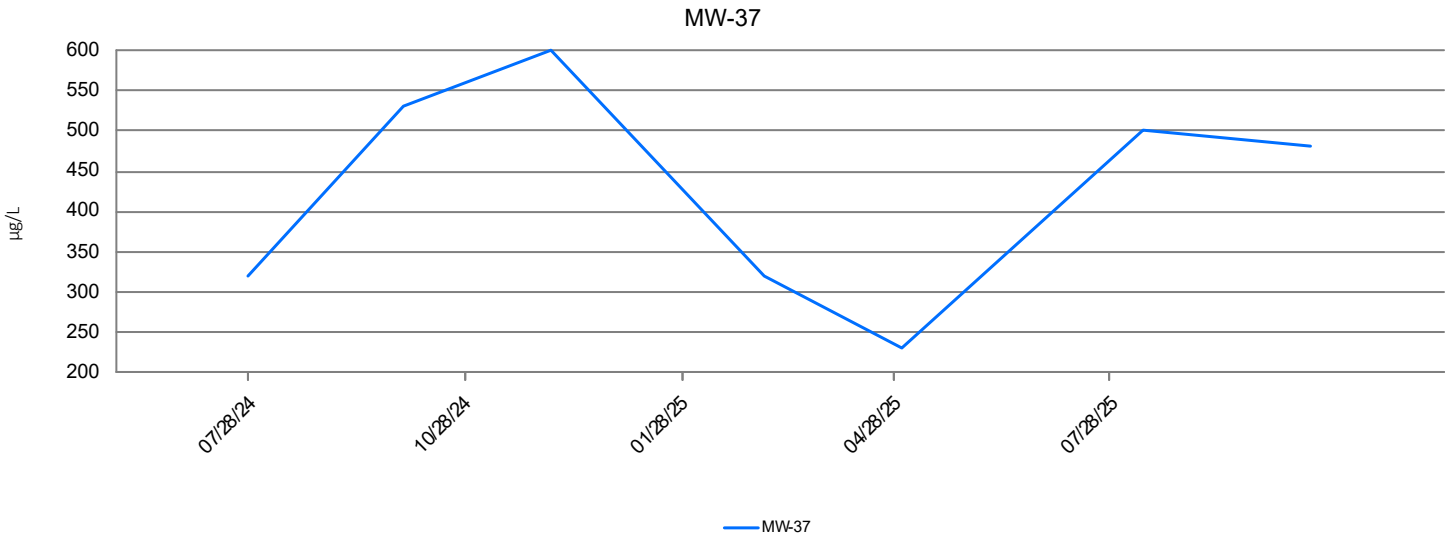


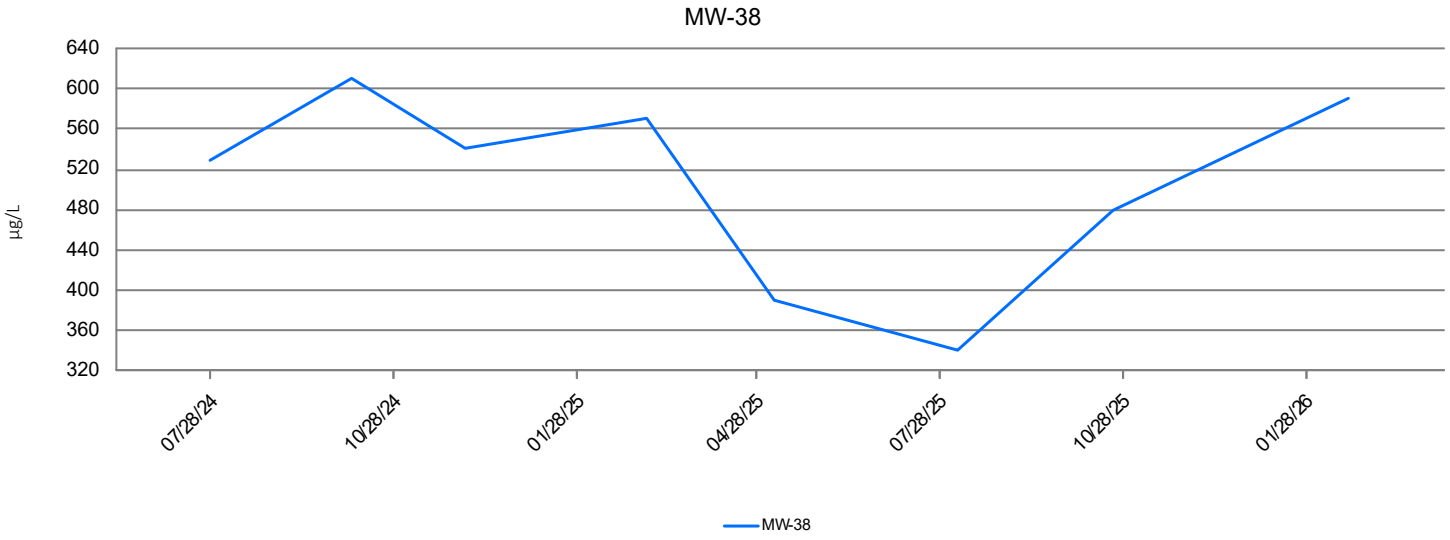
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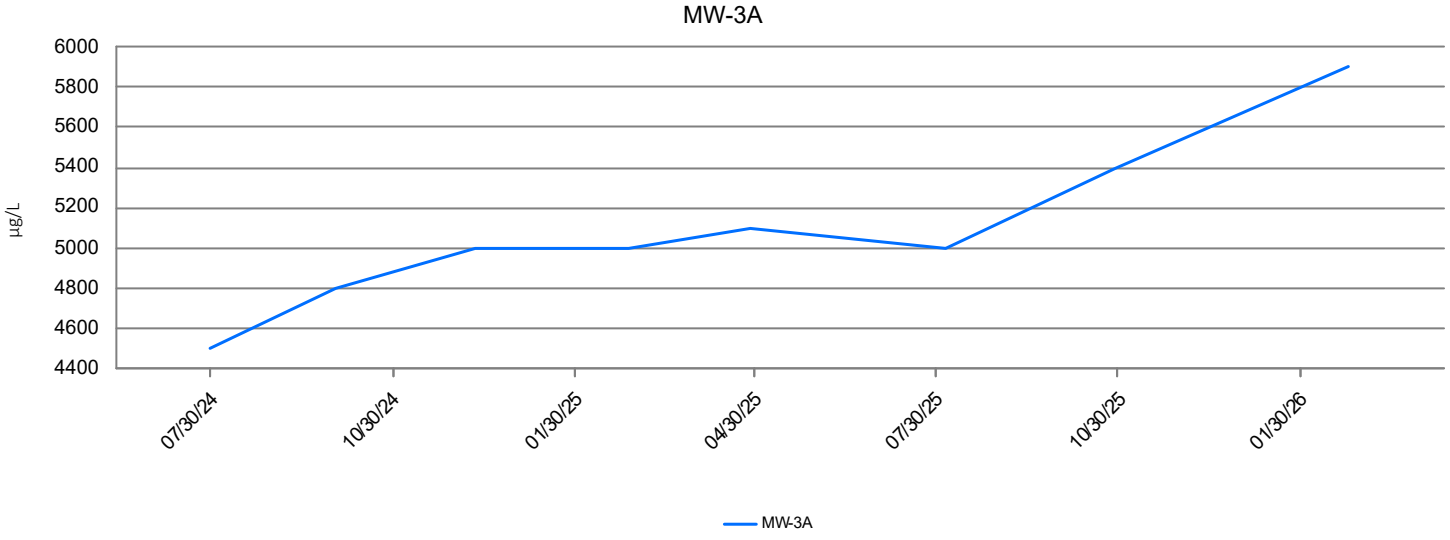
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Strontium, Total Recoverable (µg/L)







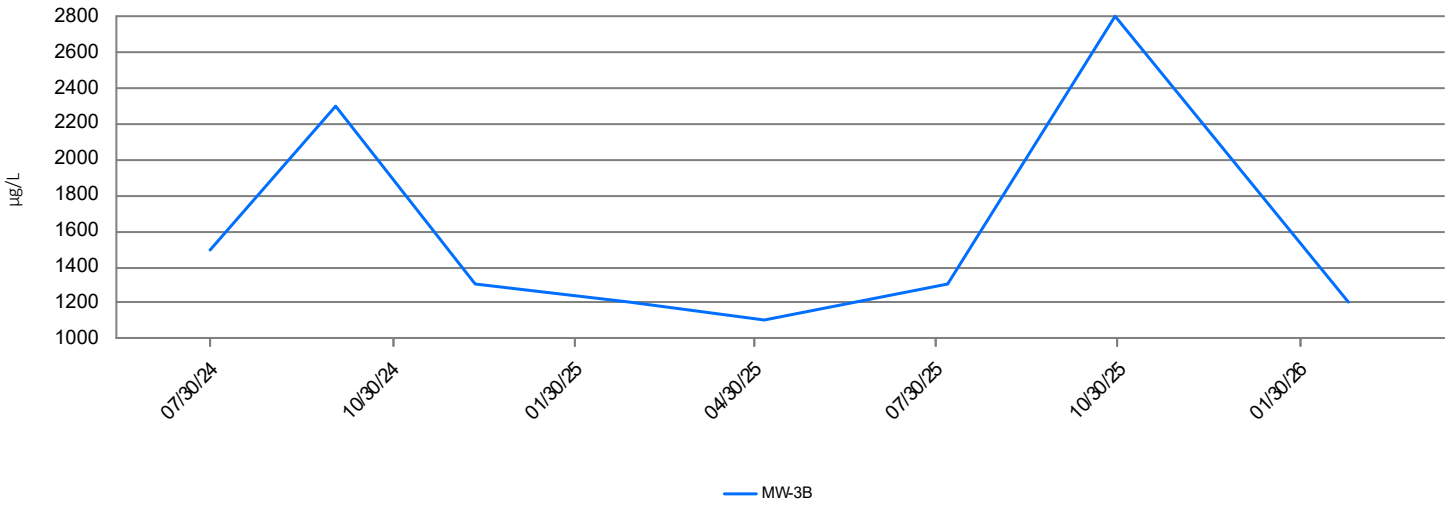
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

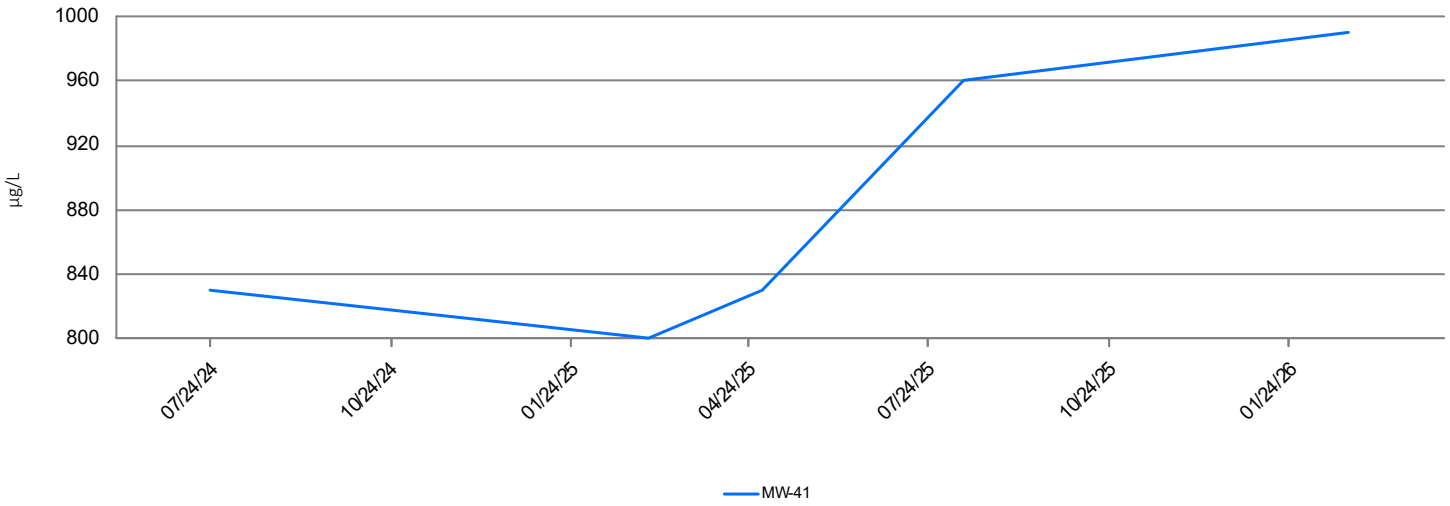
MonitorPro

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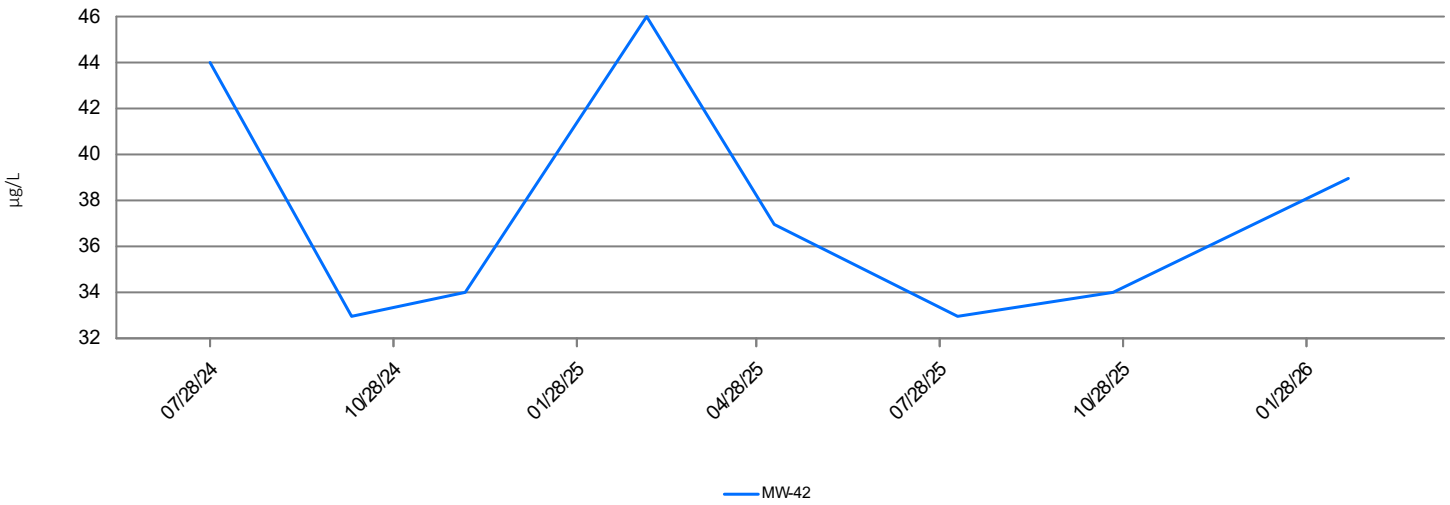
MW-3B



MW-41



MW-42

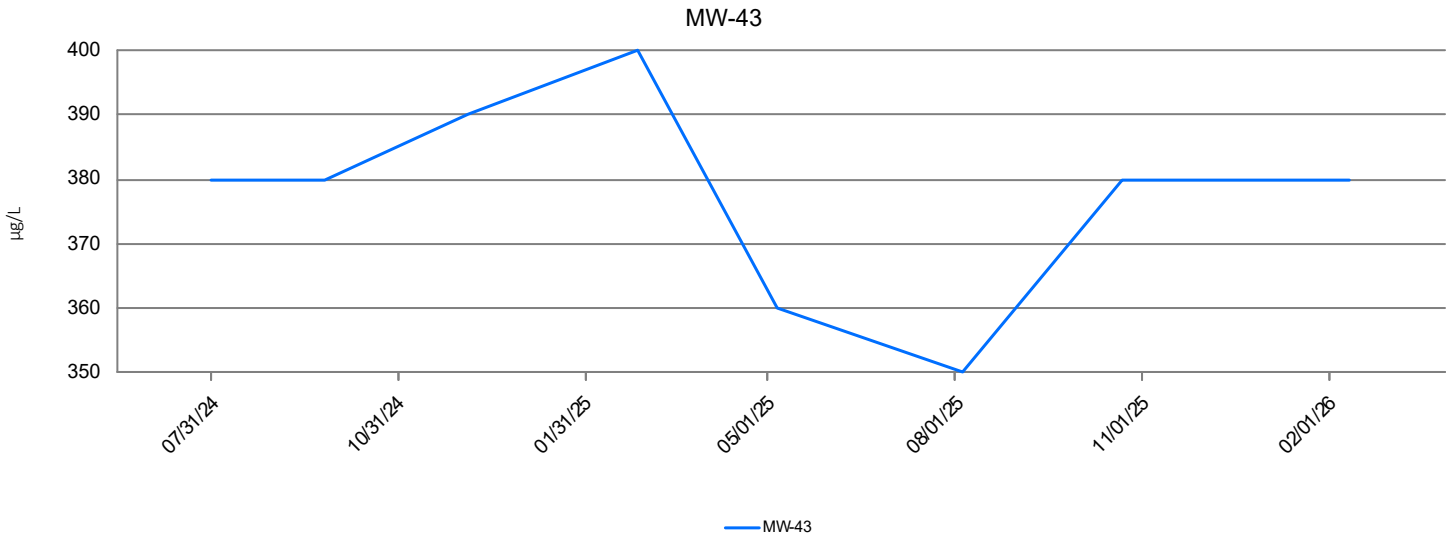


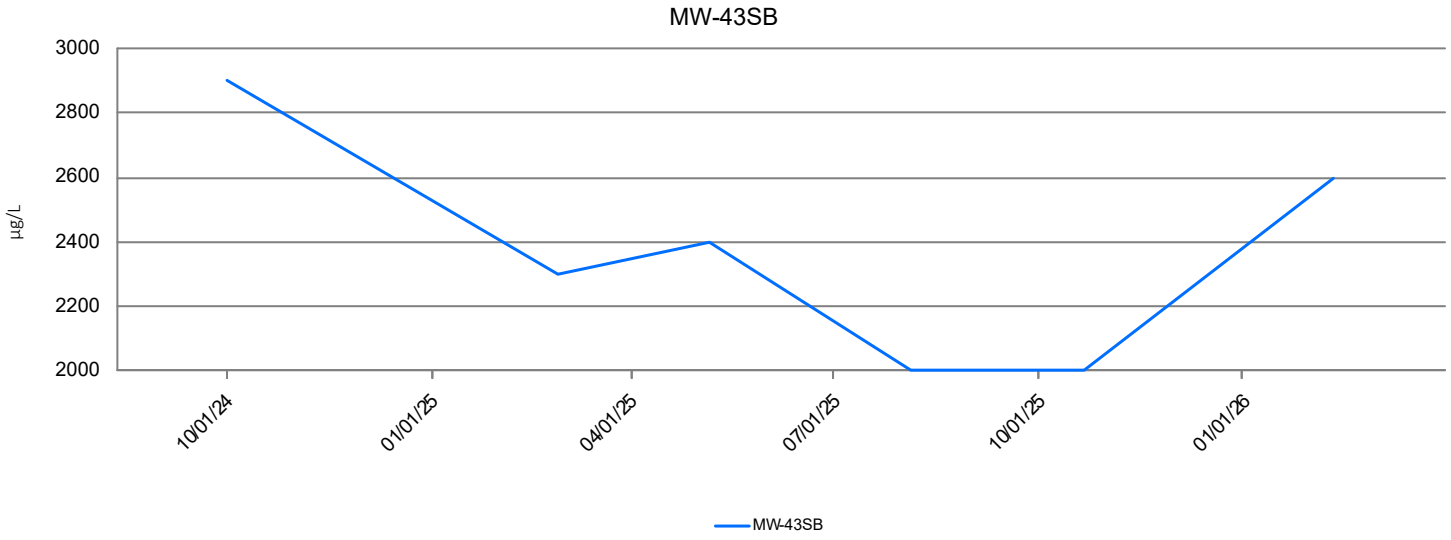
Variable Graphical Report

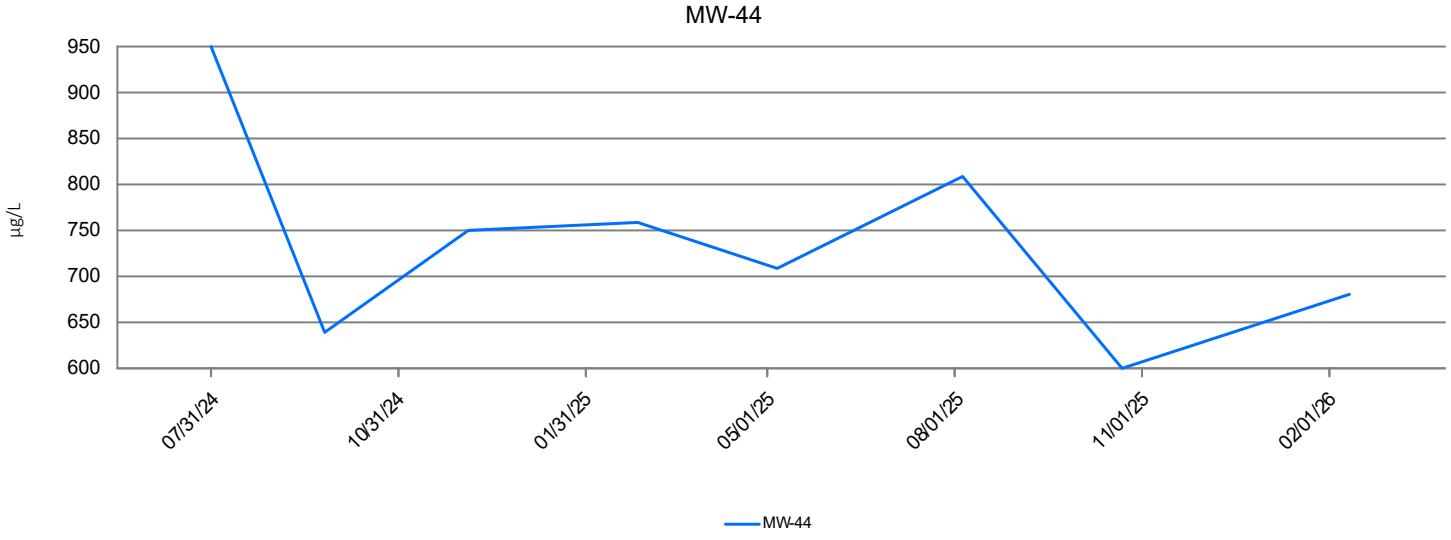
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Strontium, Total Recoverable (µg/L)





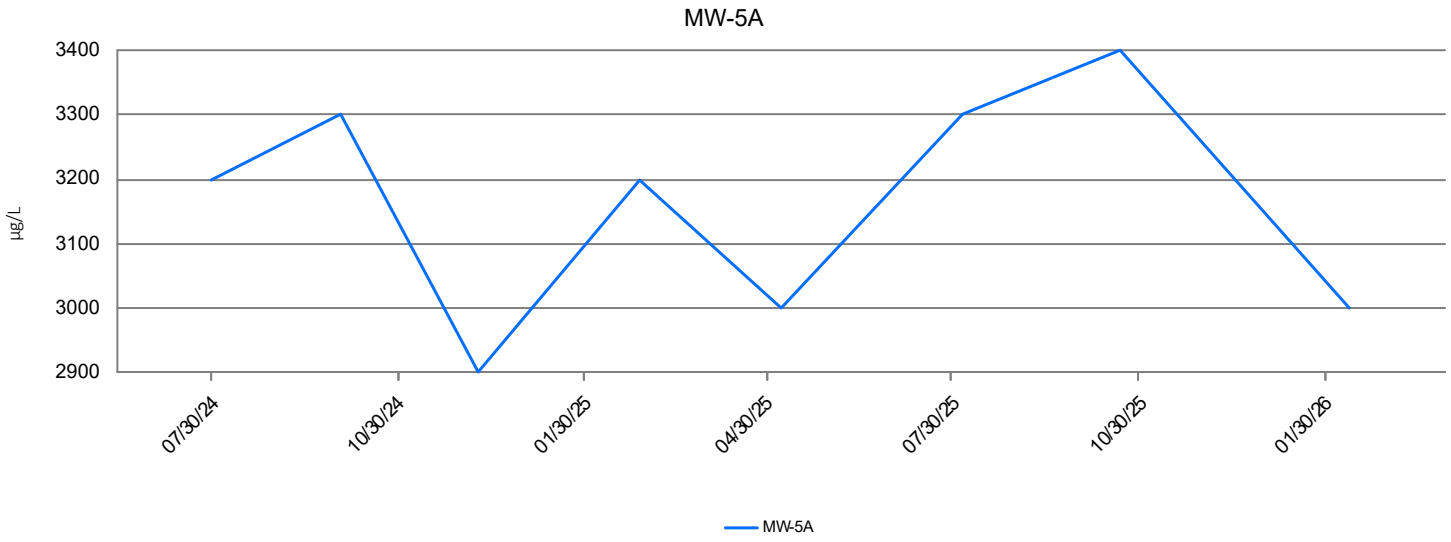


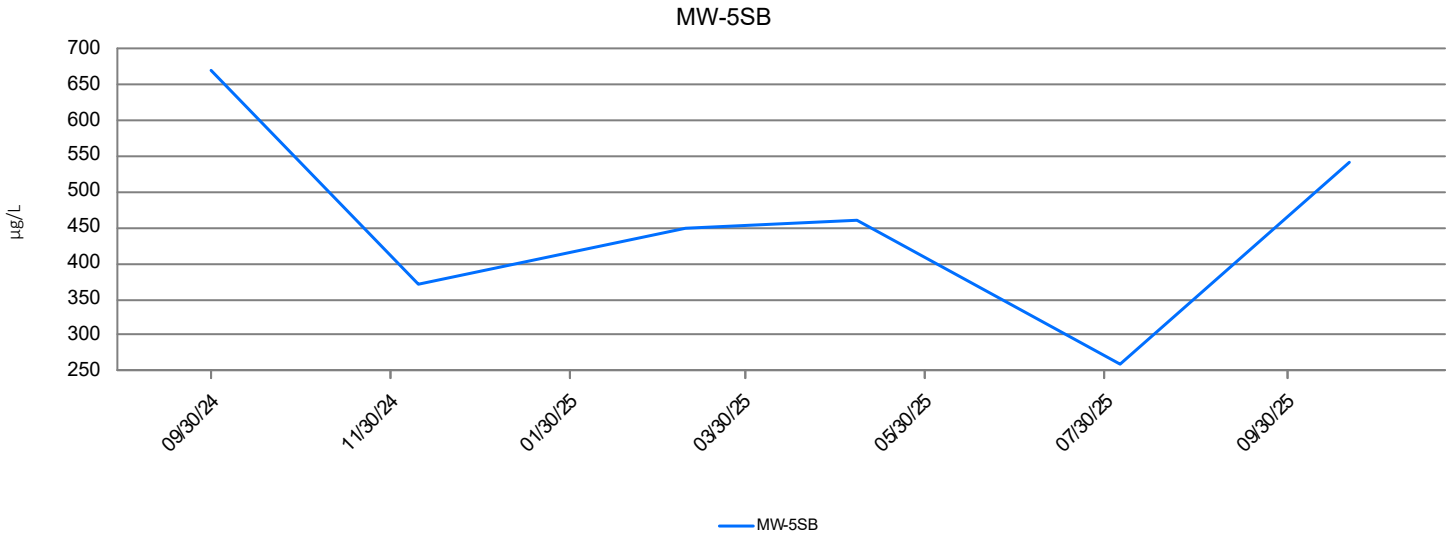
Variable Graphical Report

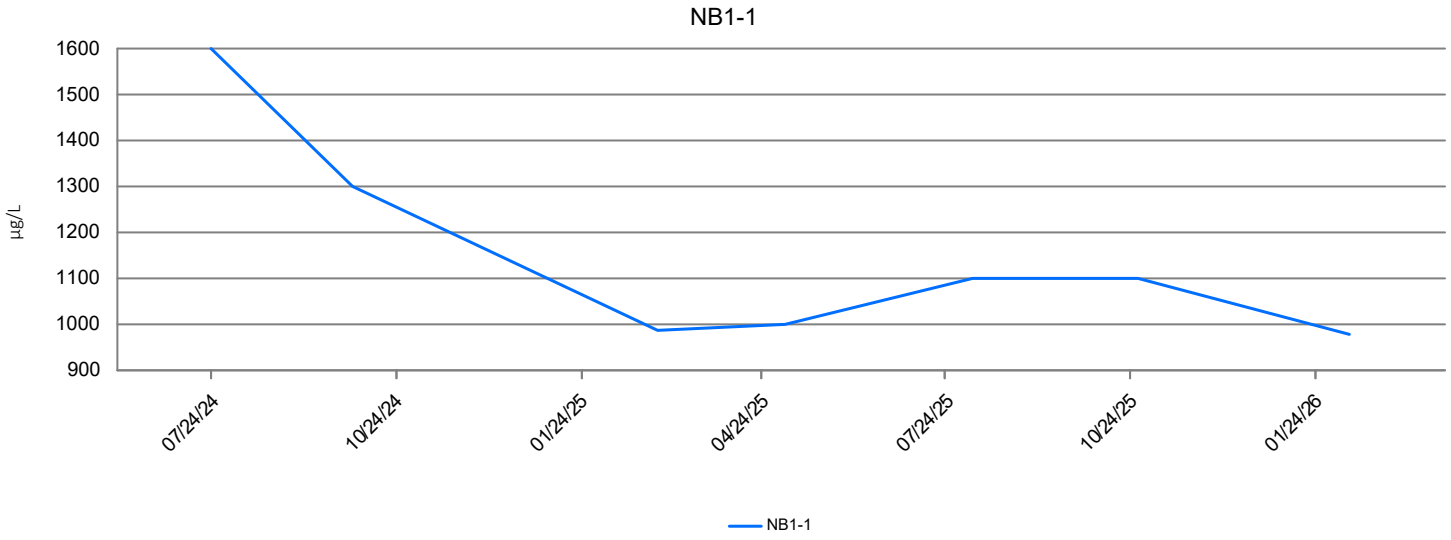
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Strontium, Total Recoverable (µg/L)





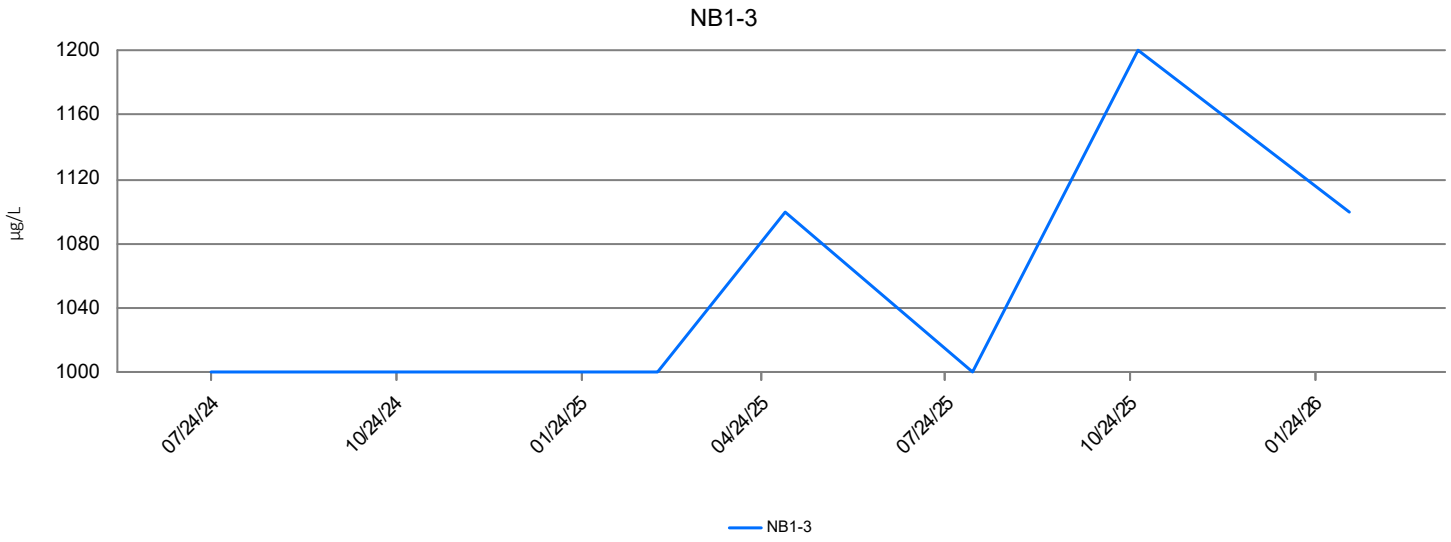


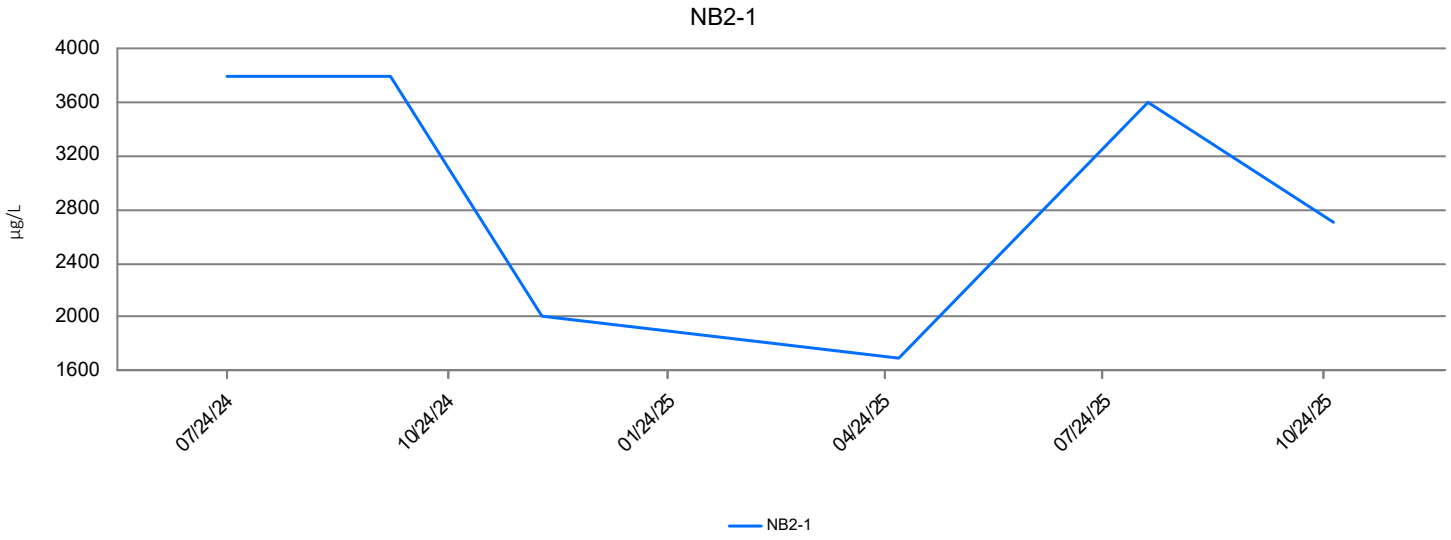
Variable Graphical Report

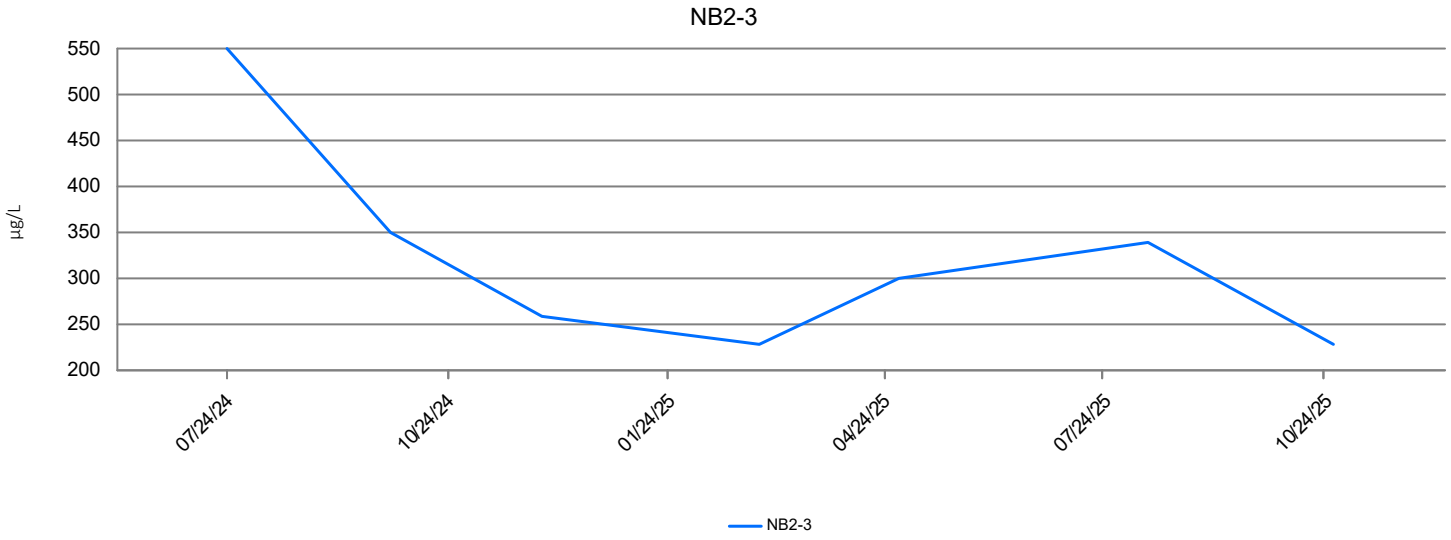
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Strontium, Total Recoverable (µg/L)





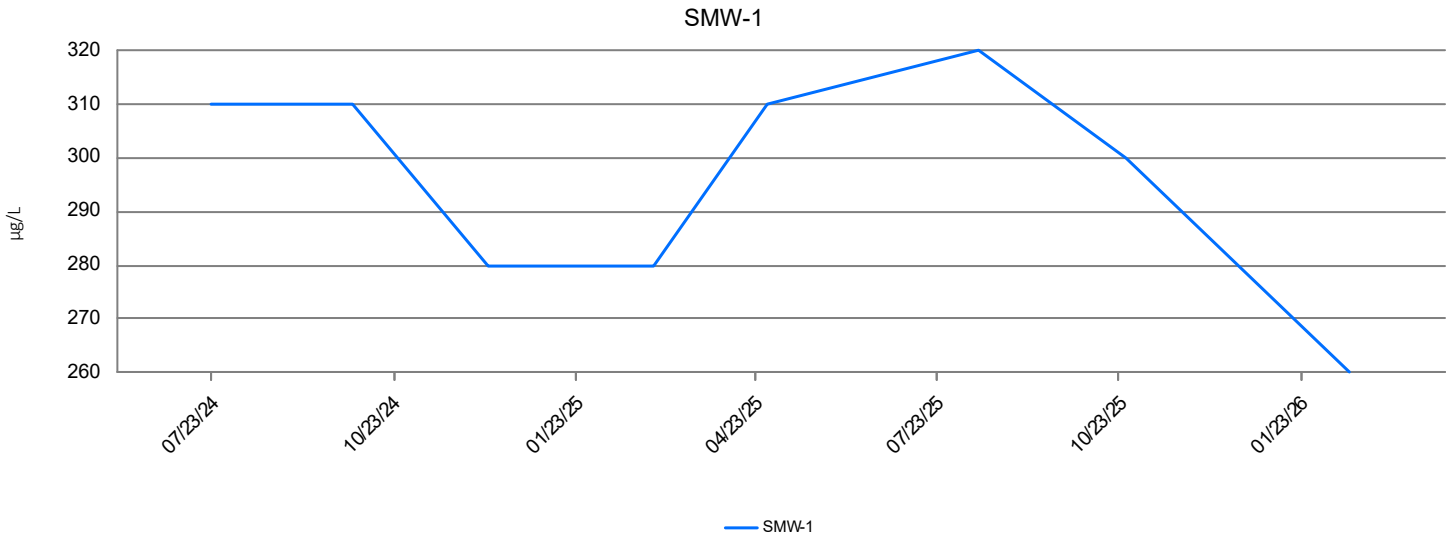


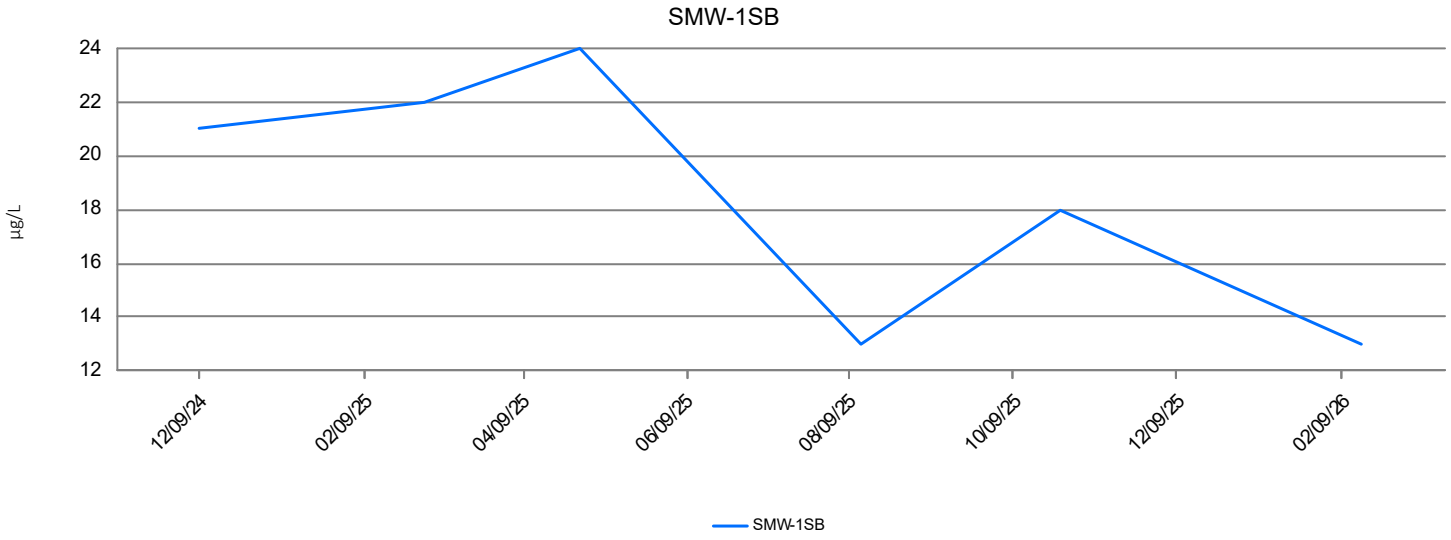
Variable Graphical Report

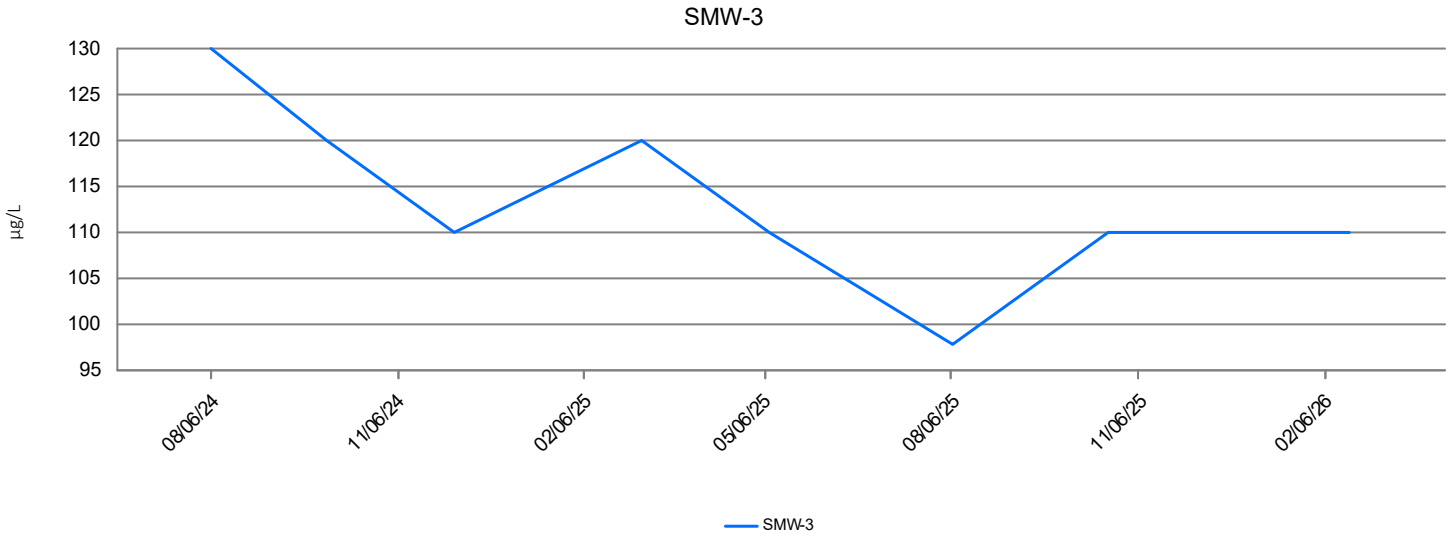
Date from 07/01/2024 to 05/01/2026

MonitorPro

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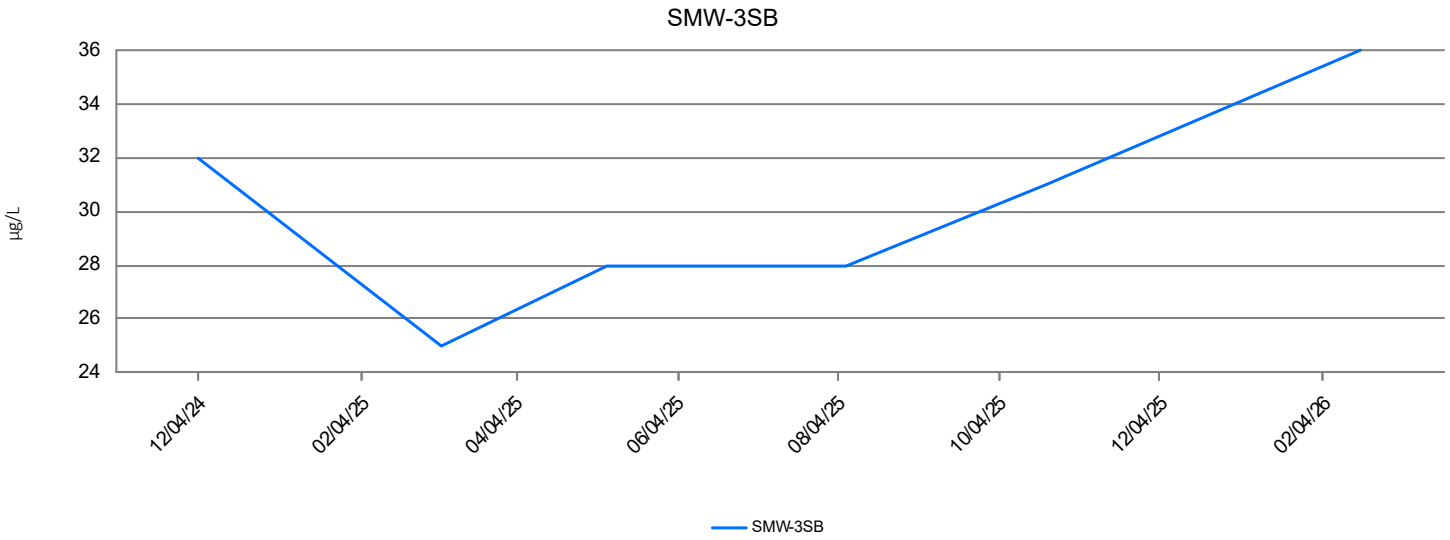


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Strontium, Total Recoverable (µg/L)

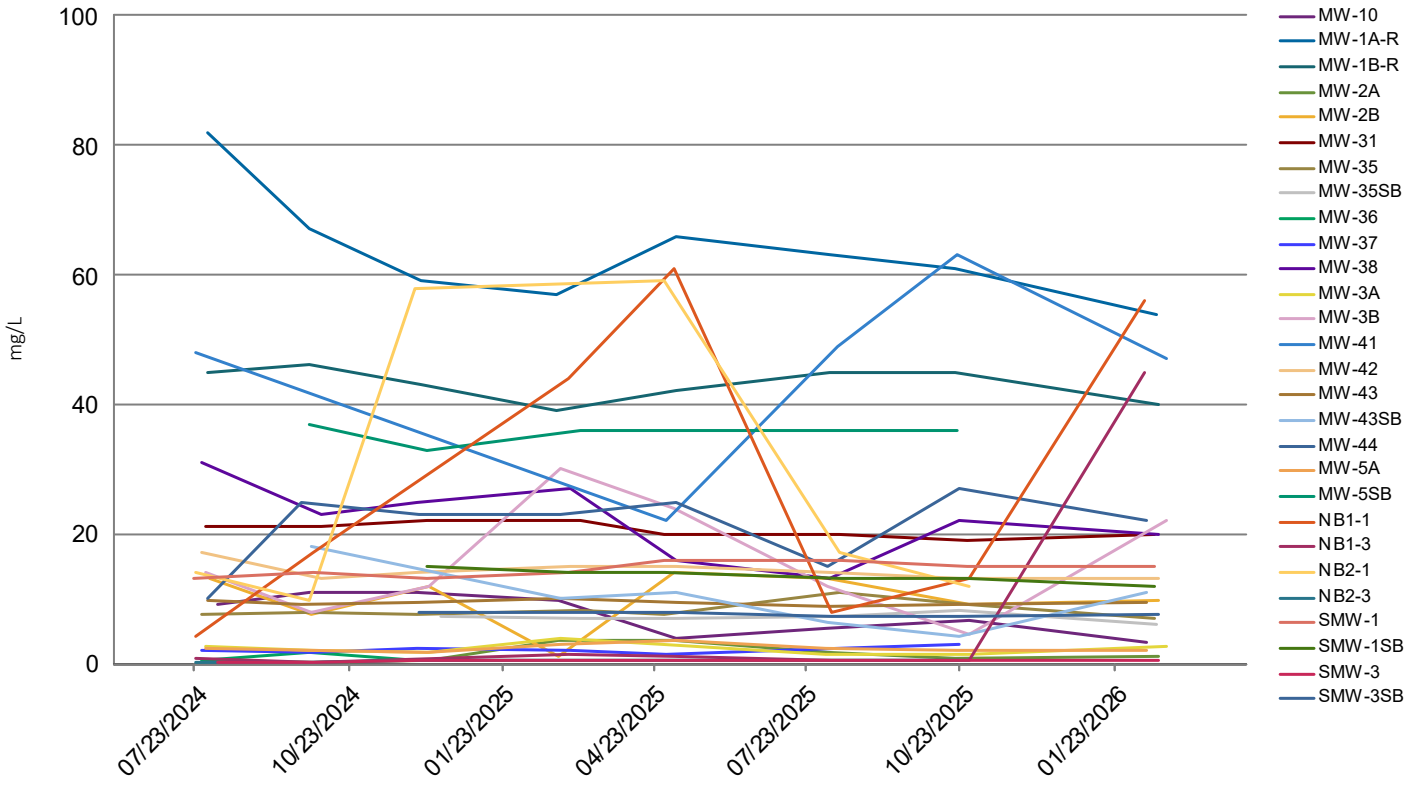


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sulfate (mg/L)

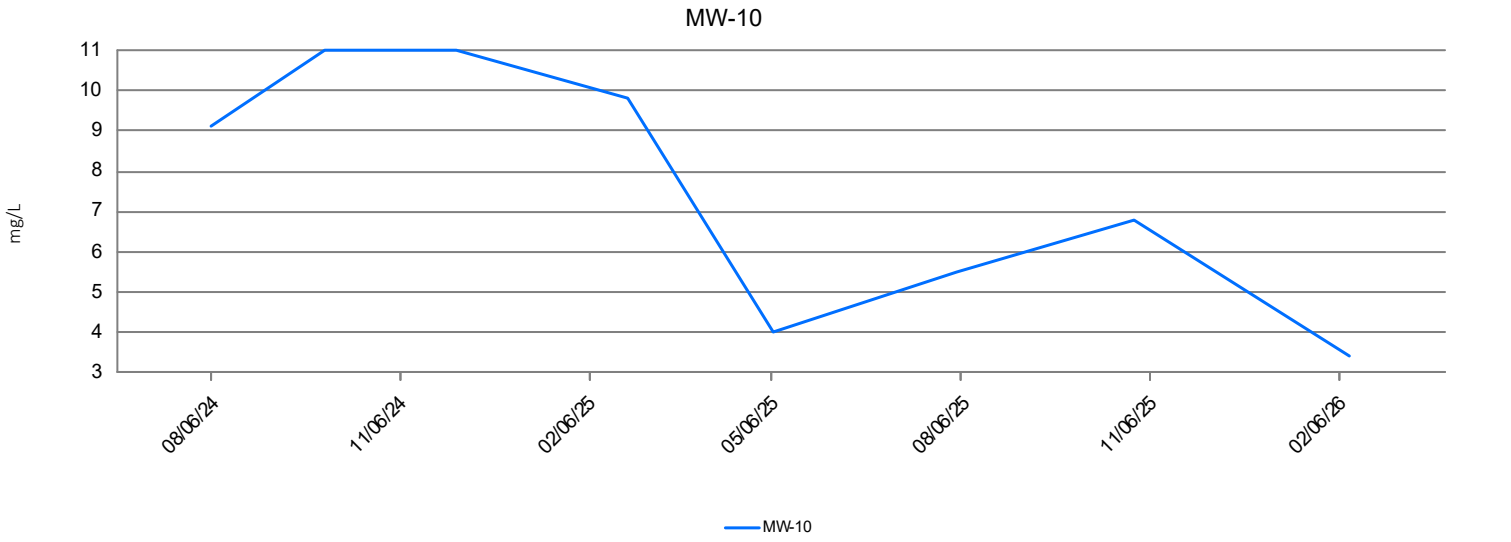


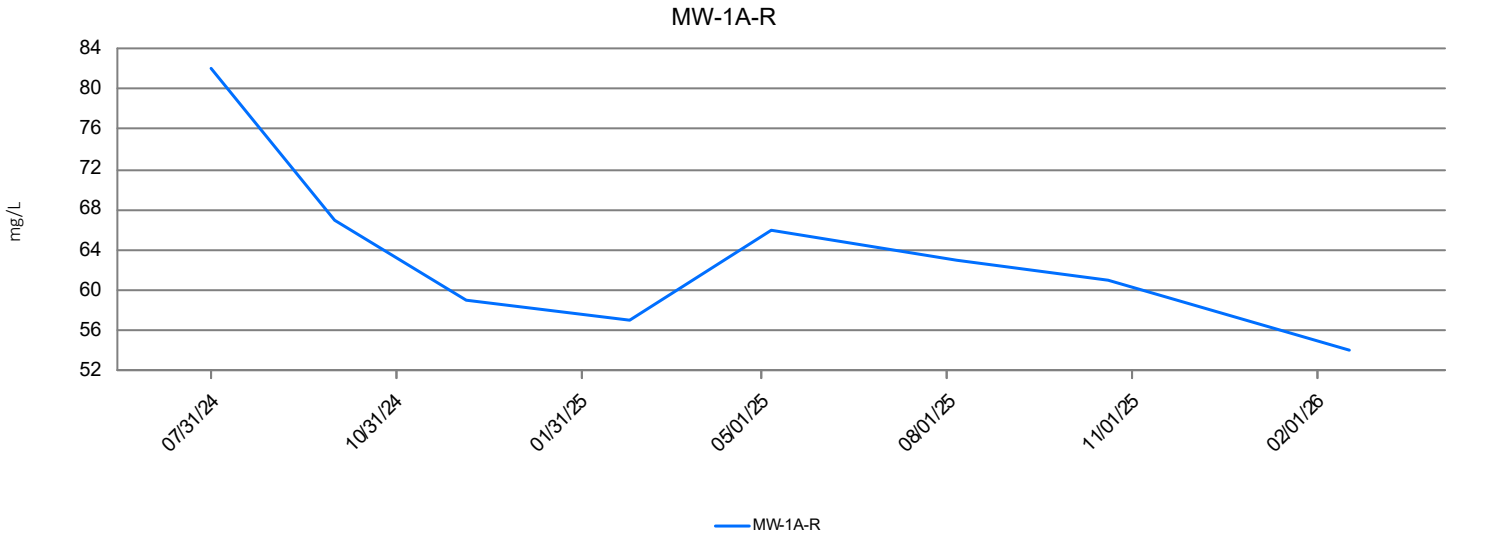
Variable Graphical Report

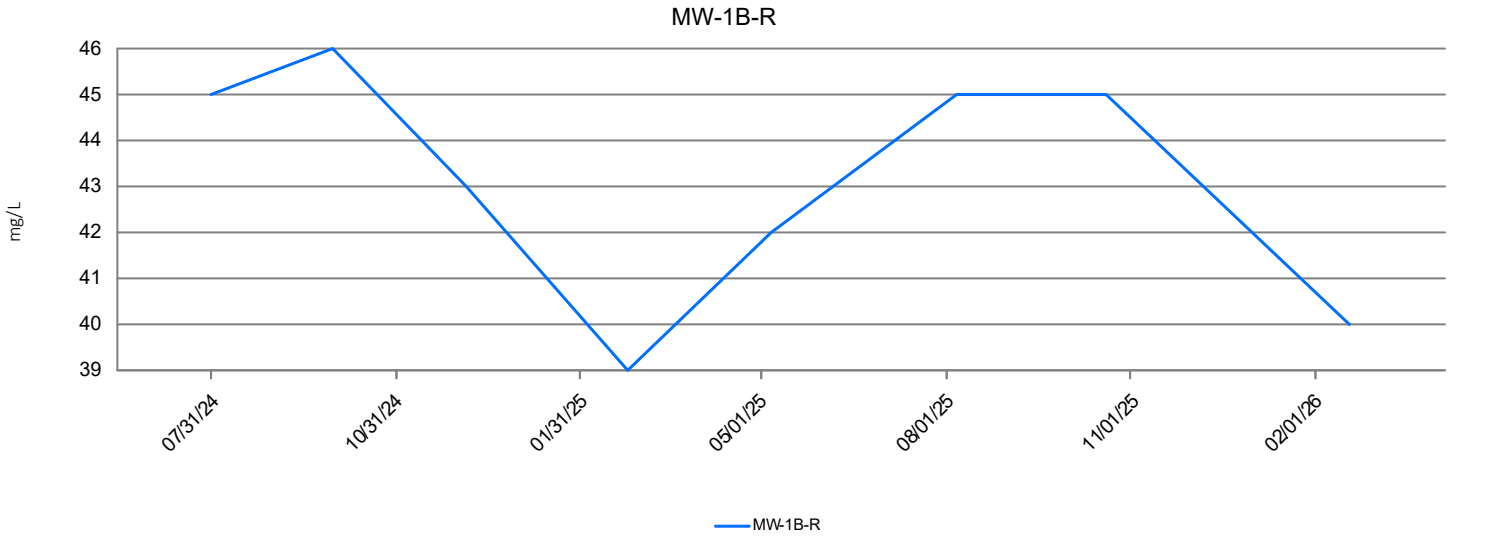
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sulfate (mg/L)







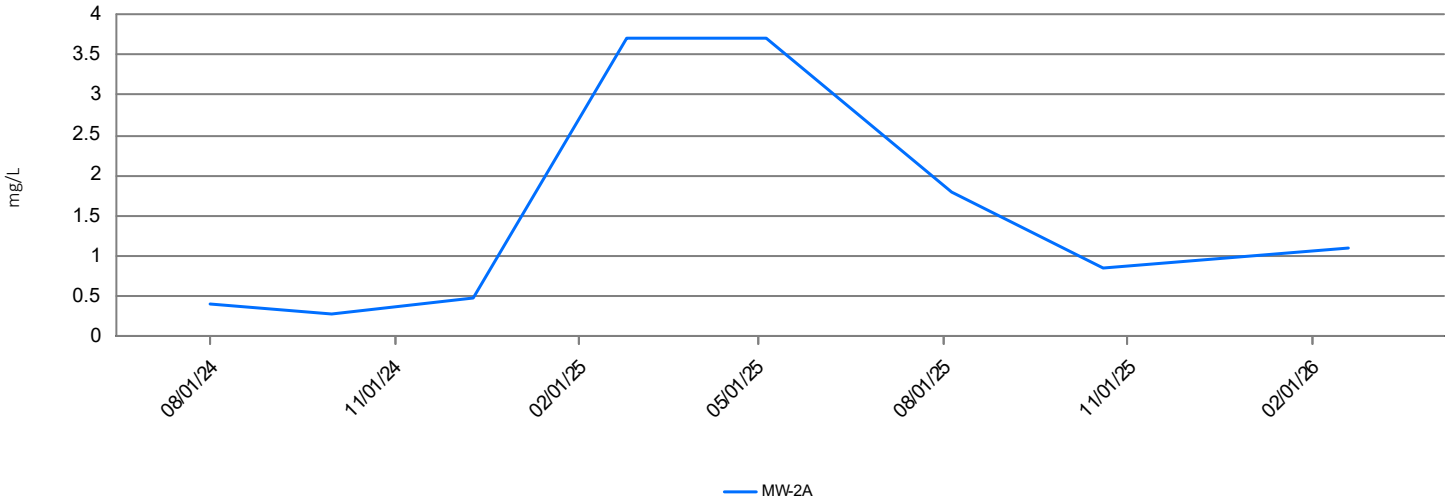
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Date from 07/01/2024 to 05/01/2026

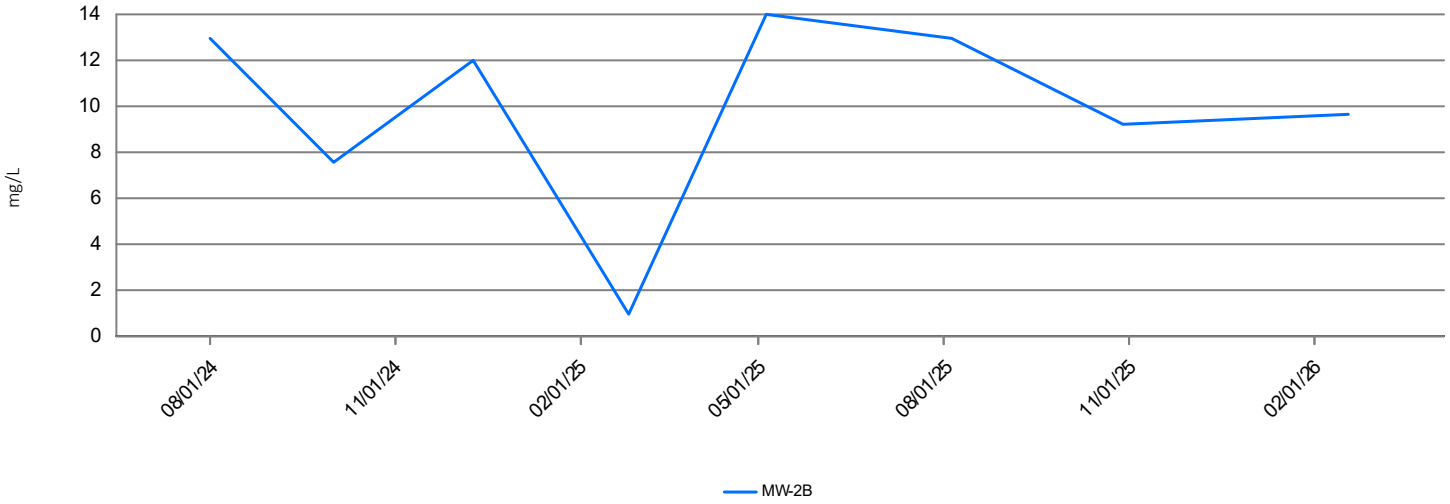
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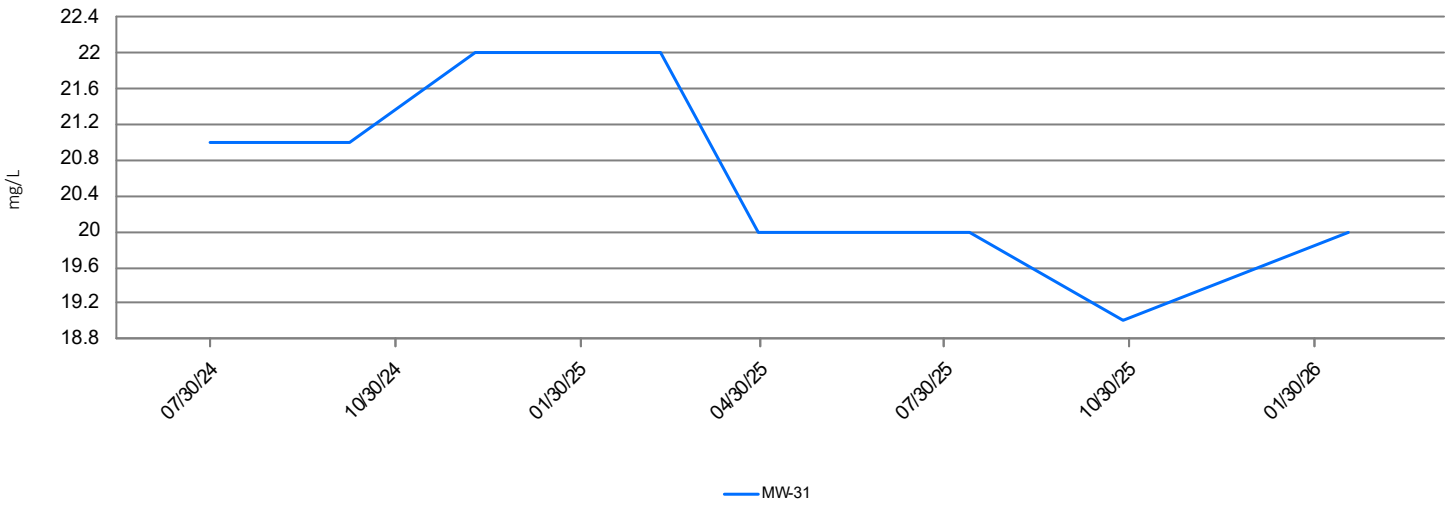
MW-2A



MW-2B



MW-31

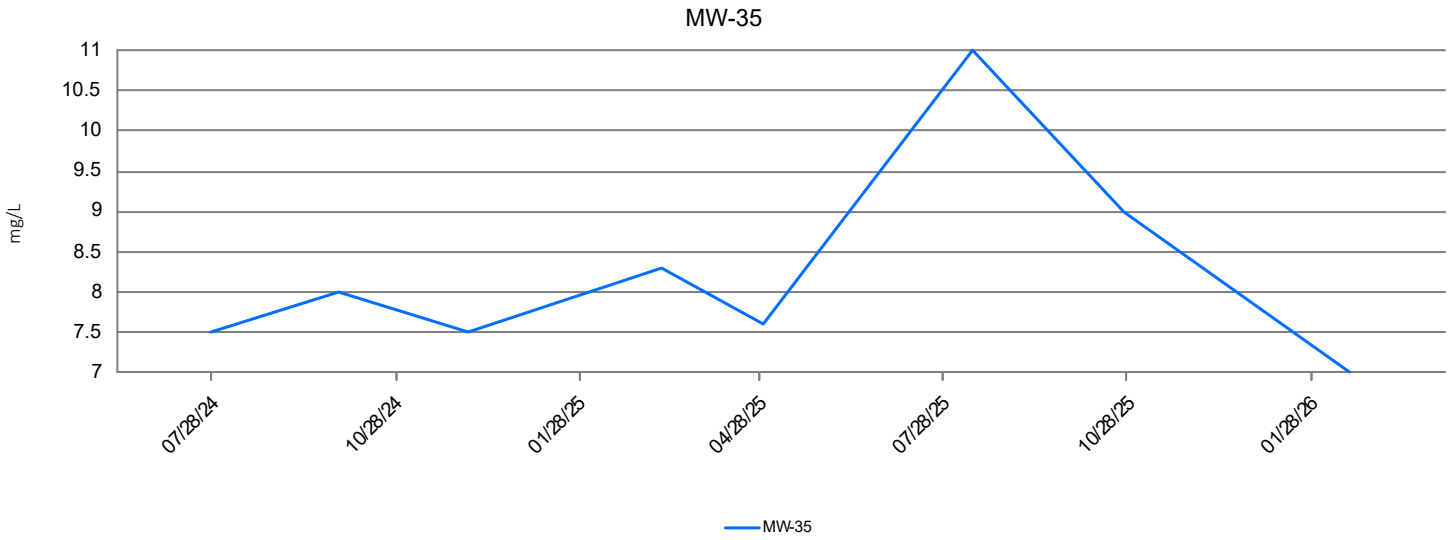


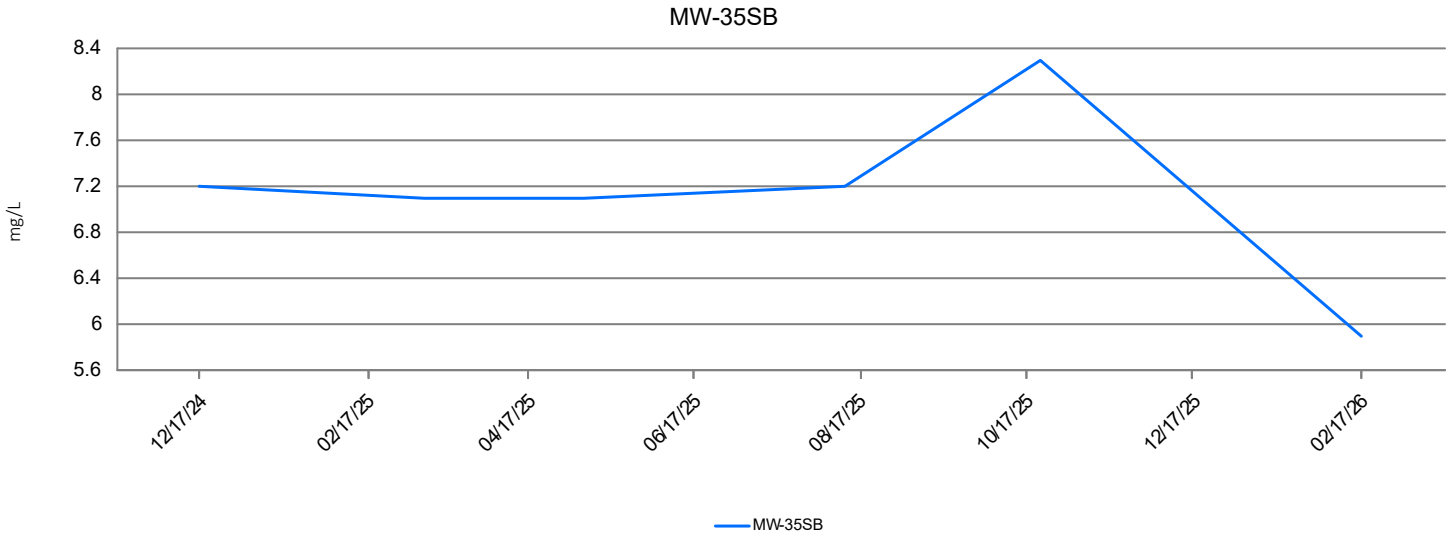
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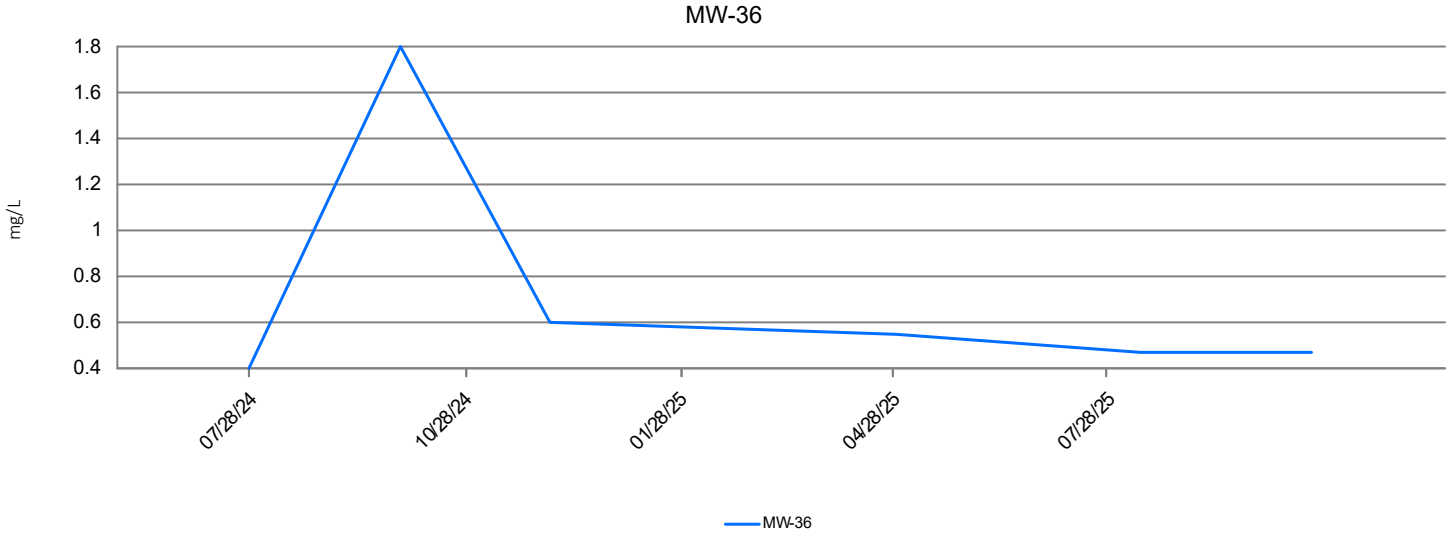
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sulfate (mg/L)







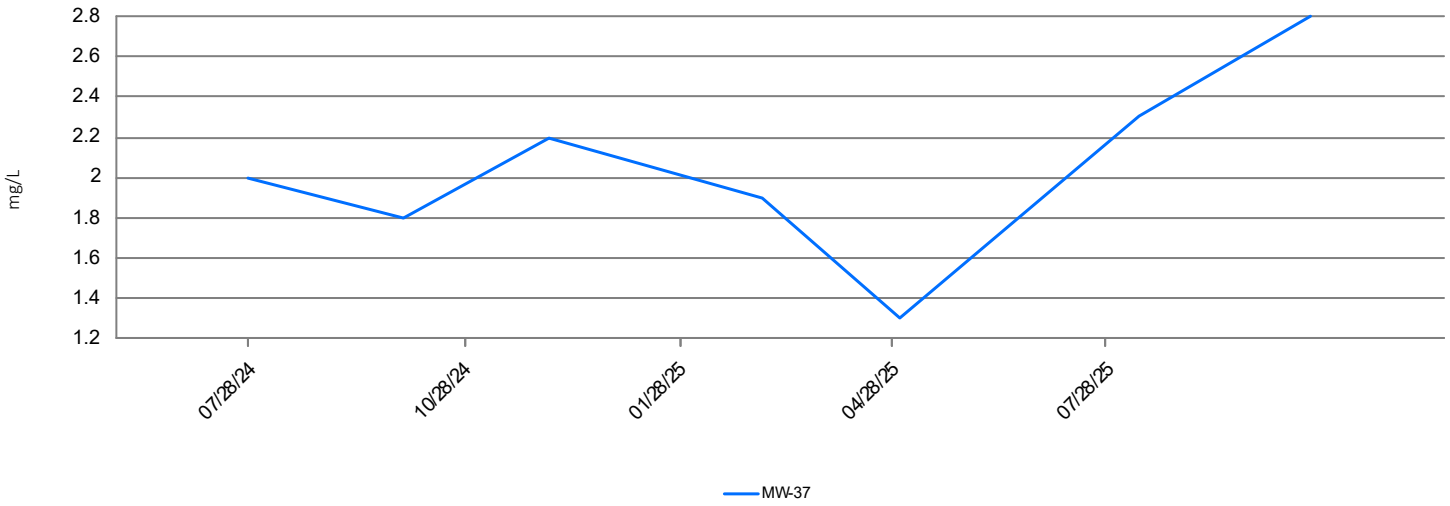
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

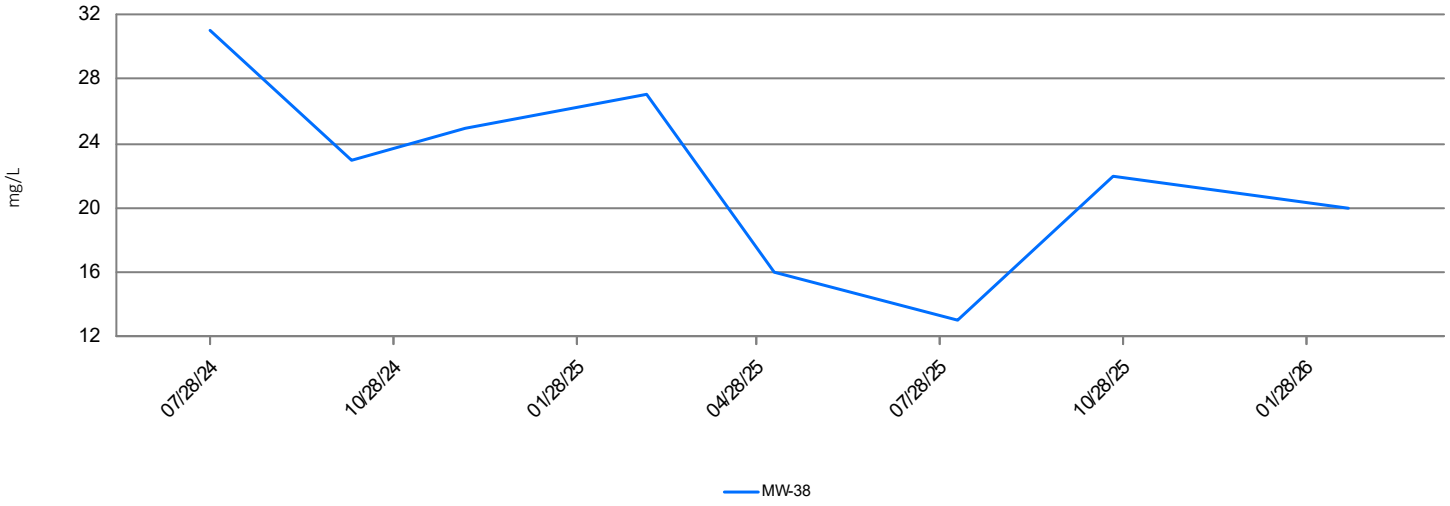
MonitorPro

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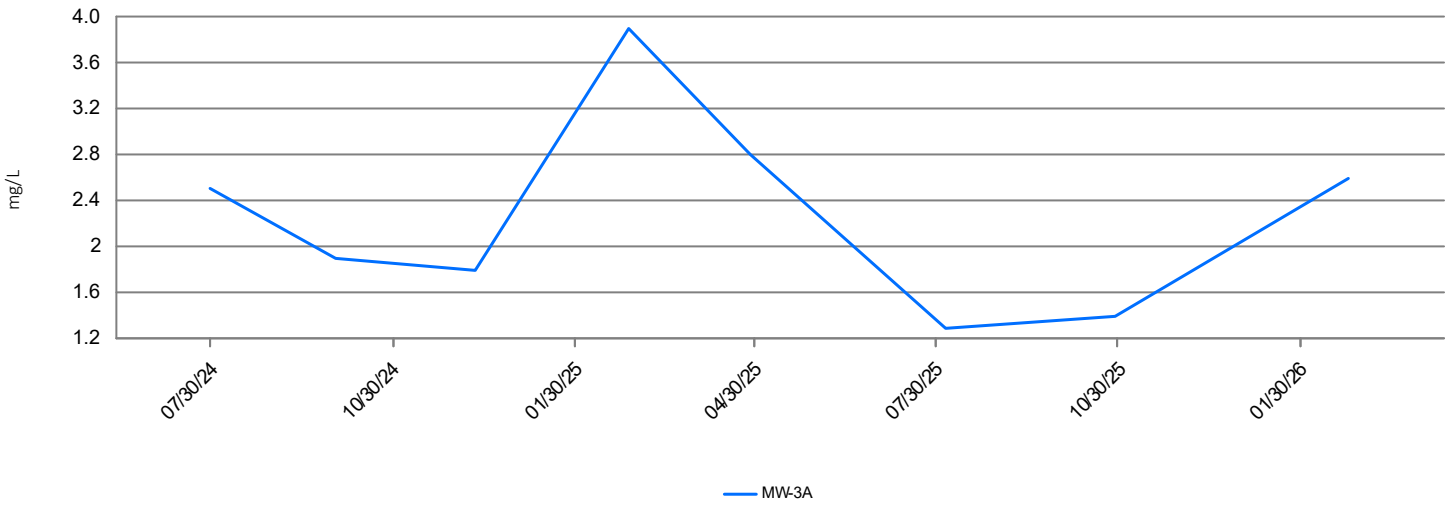
MW-37



MW-38



MW-3A

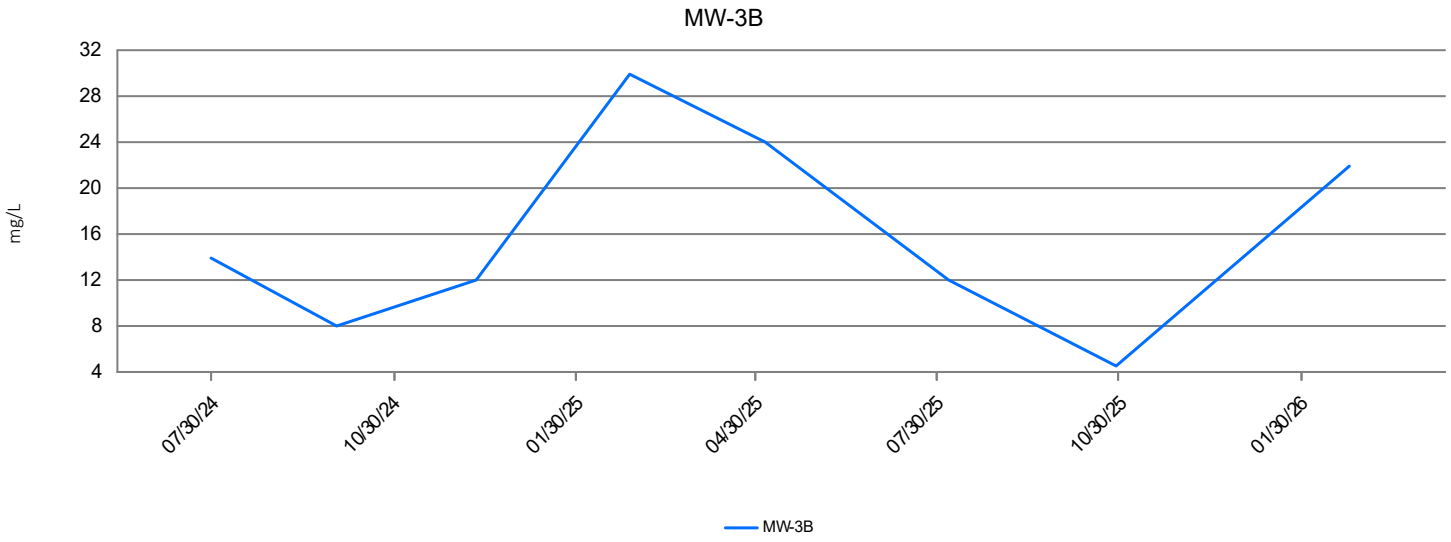


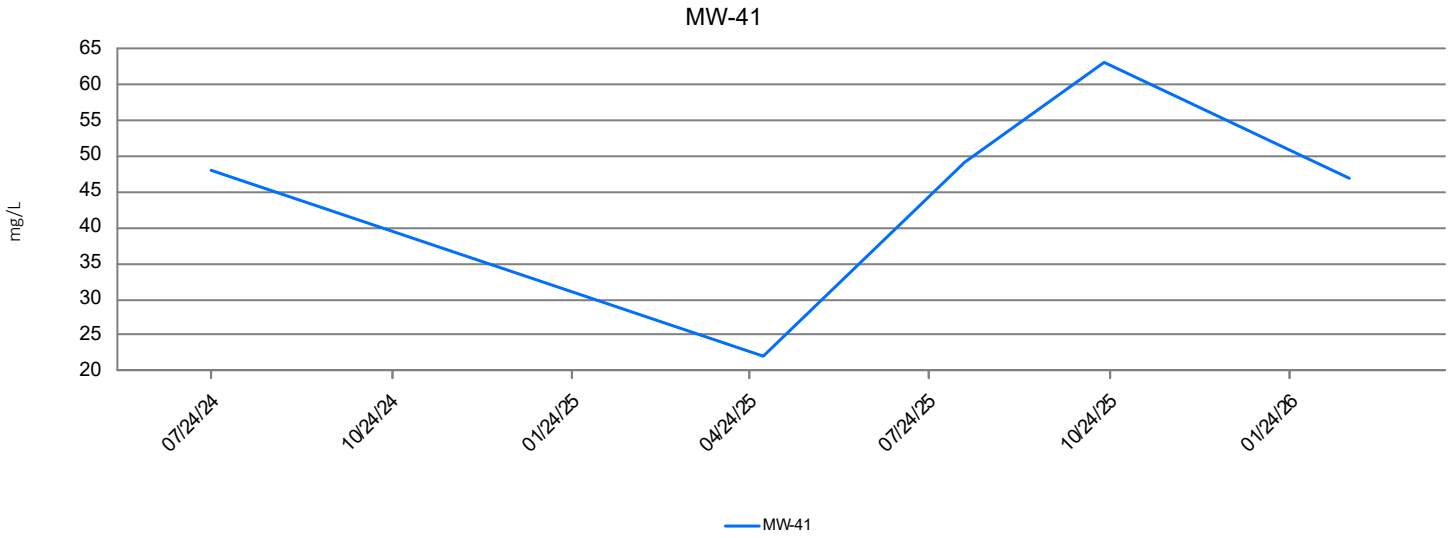
Variable Graphical Report

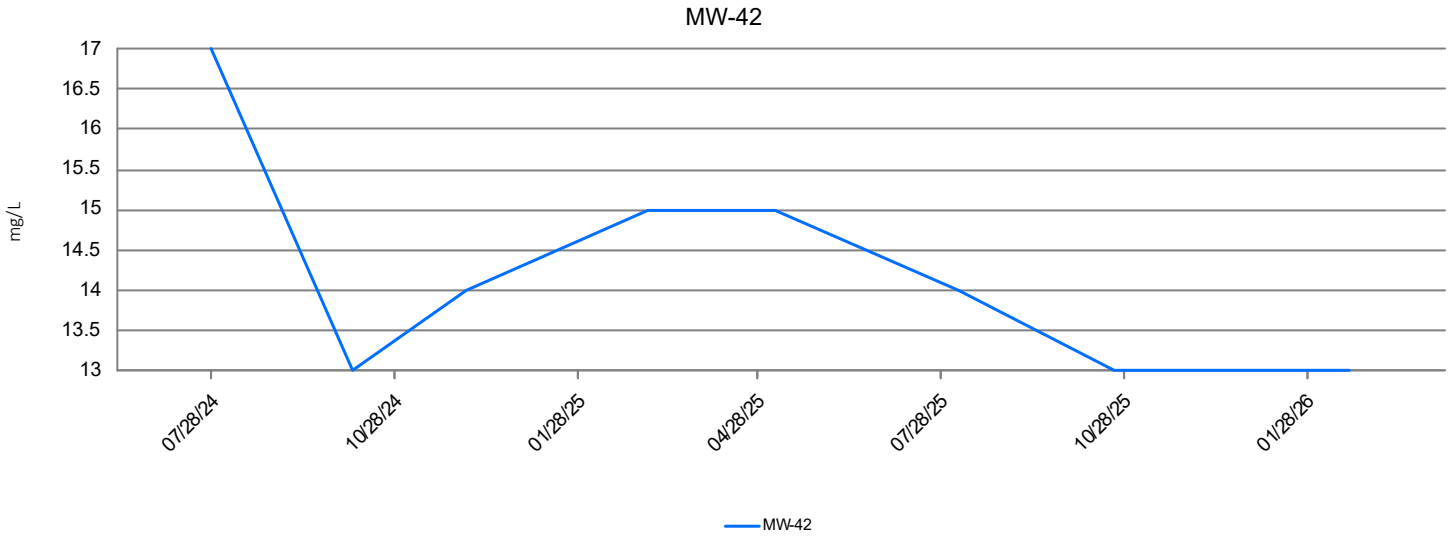
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sulfate (mg/L)





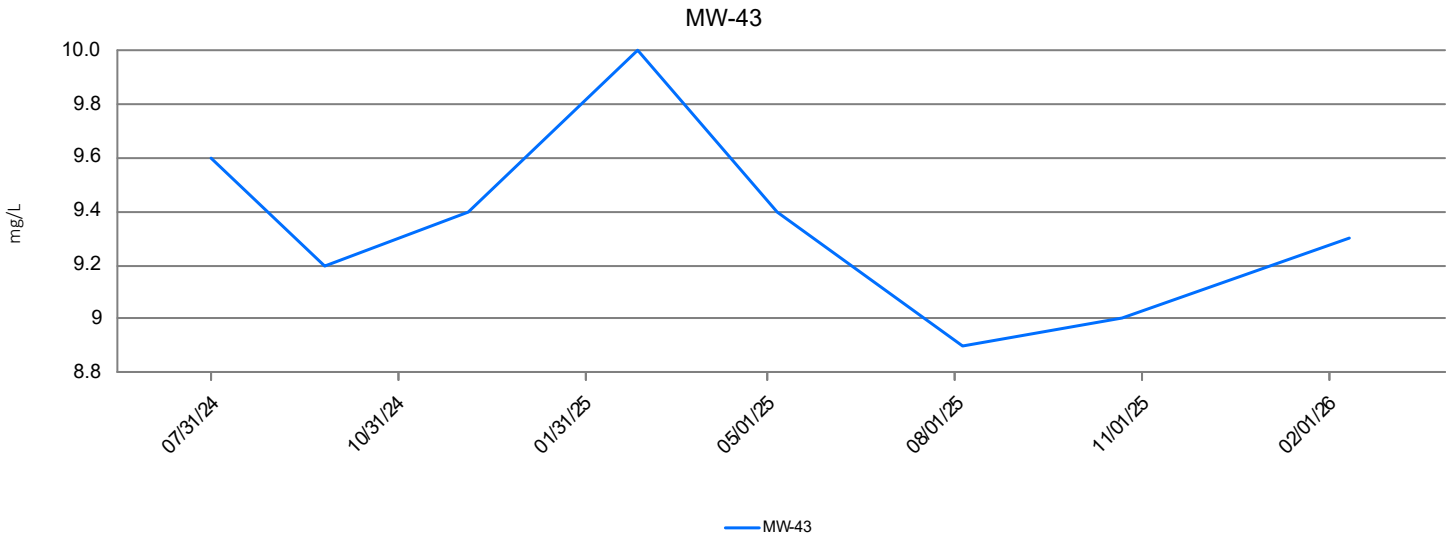


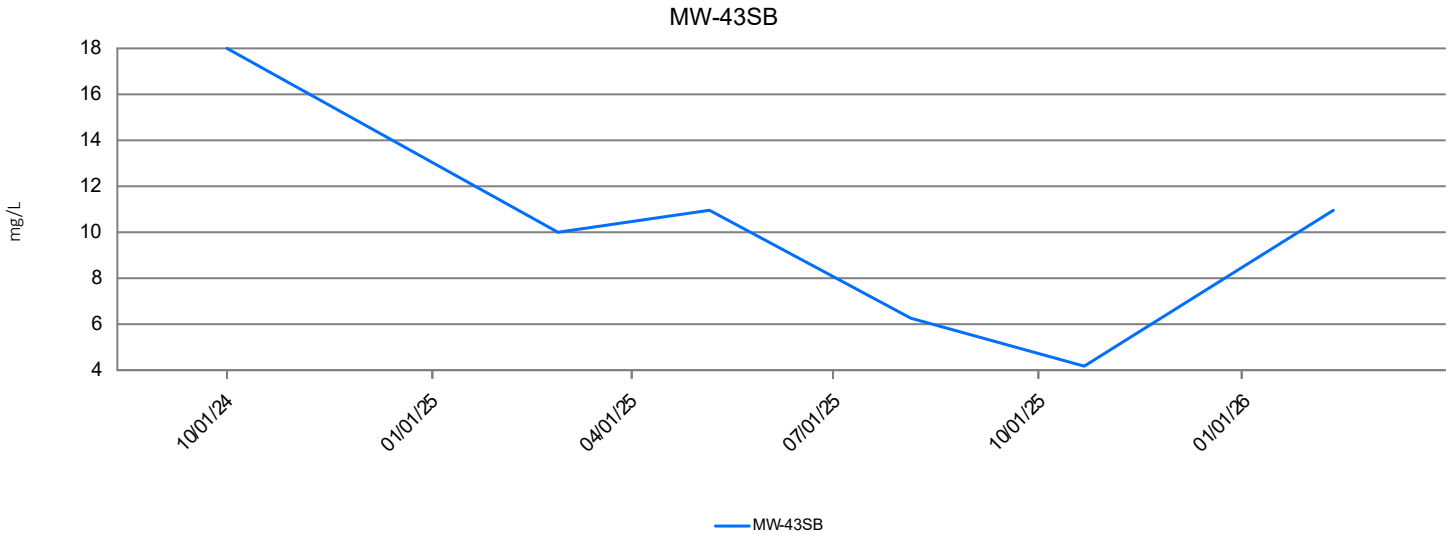
Variable Graphical Report

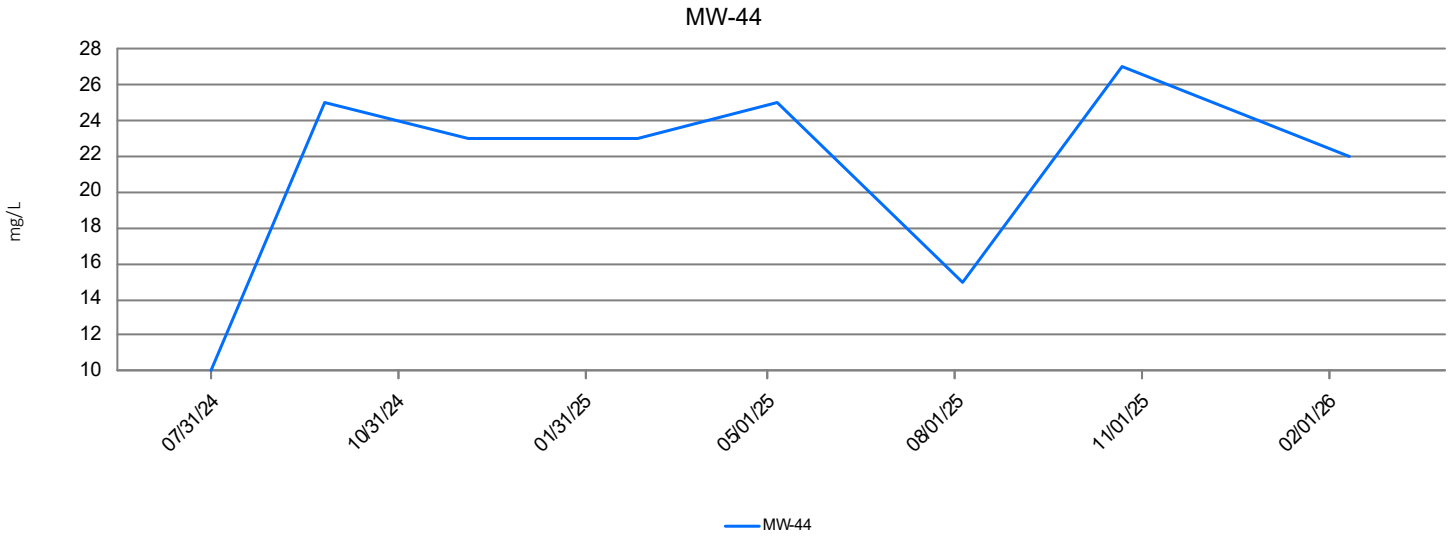
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sulfate (mg/L)







Printed Date: 05/21/2026

EHS DATA

MCERTS Cert. no. Sira MC090140/02

MCERTS

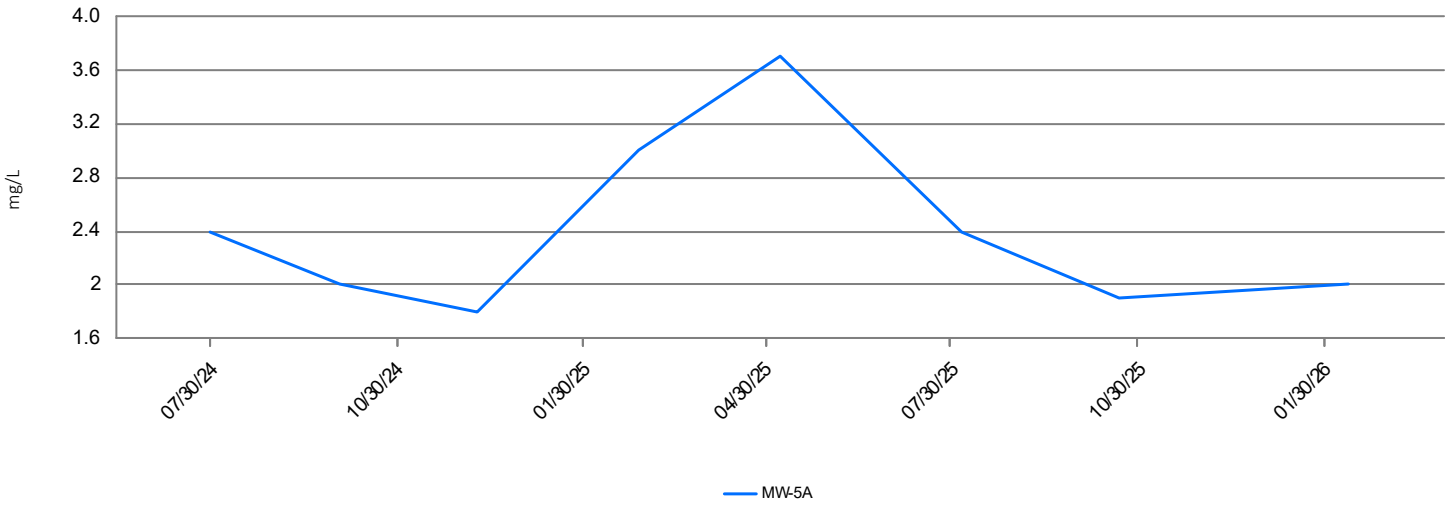
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

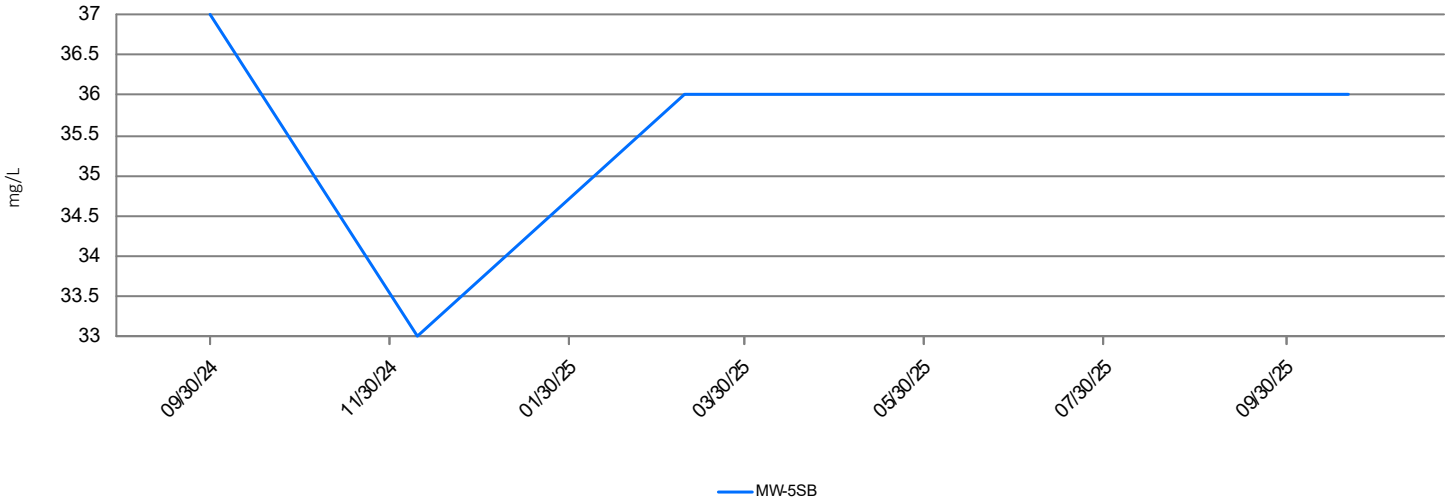
MonitorPro

No Group Selected, Sulfate (mg/L)

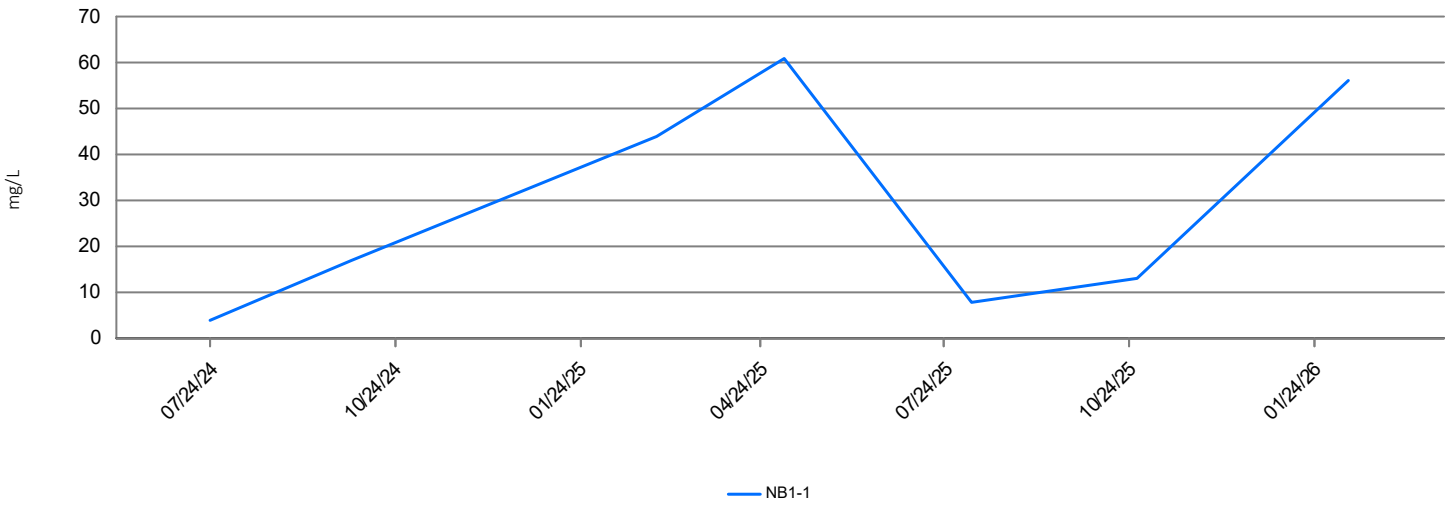
MW-5A



MW-5SB



NB1-1

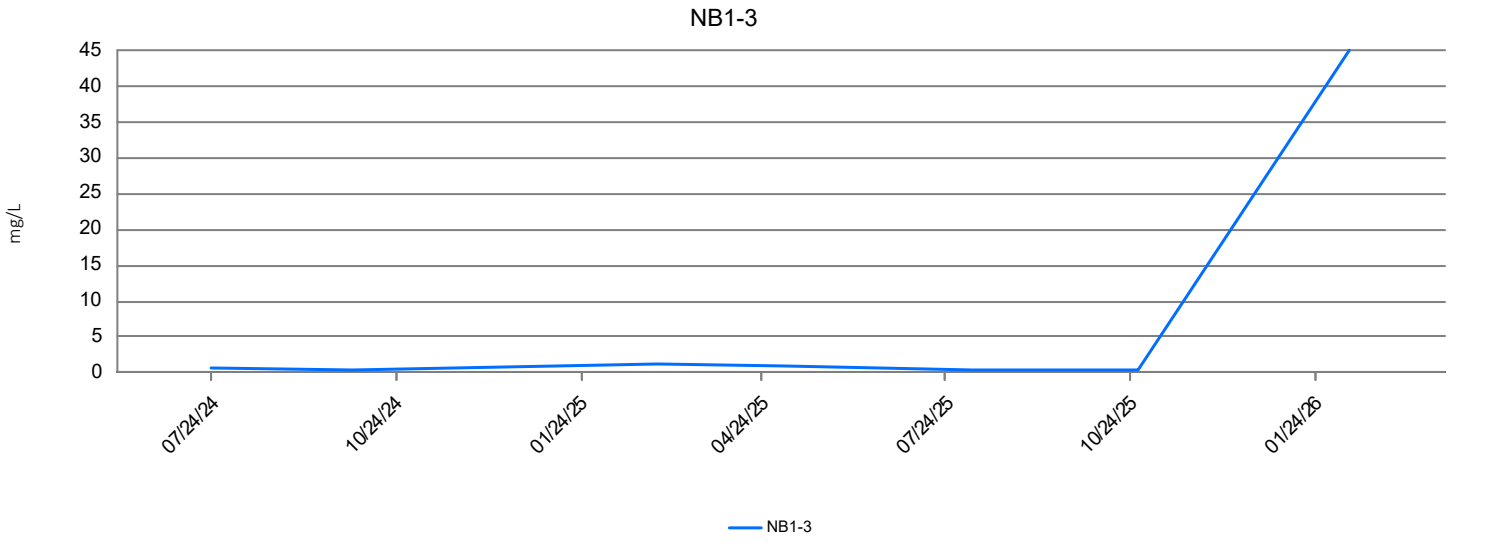


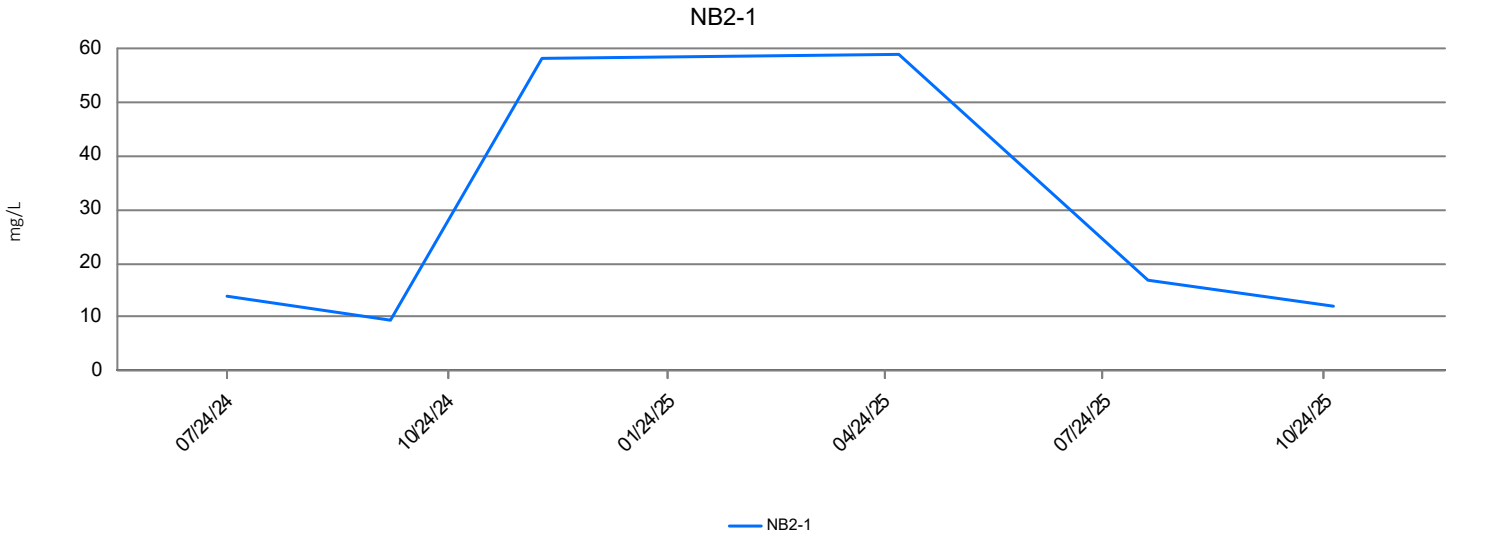
Variable Graphical Report

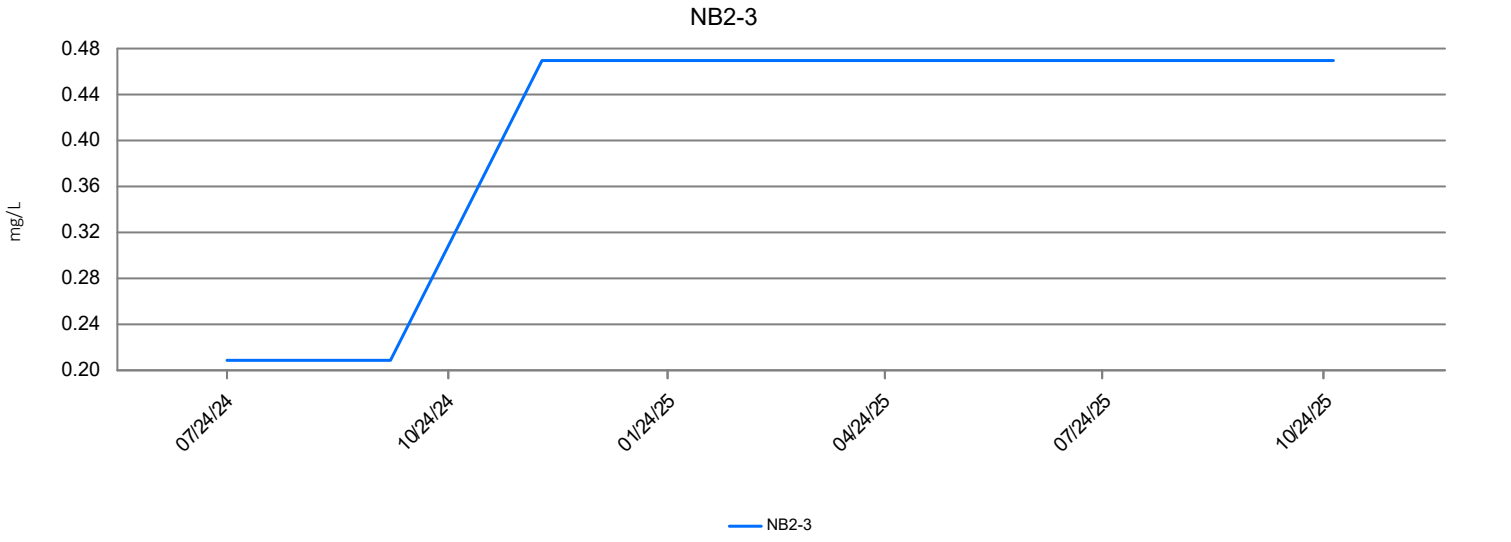
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sulfate (mg/L)







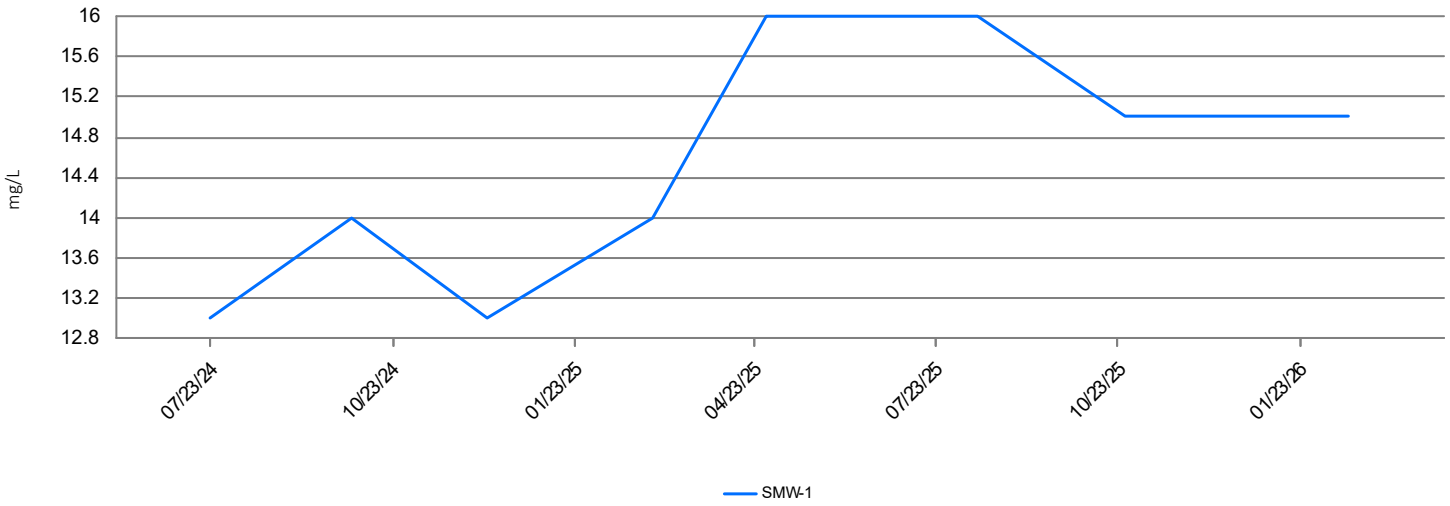
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

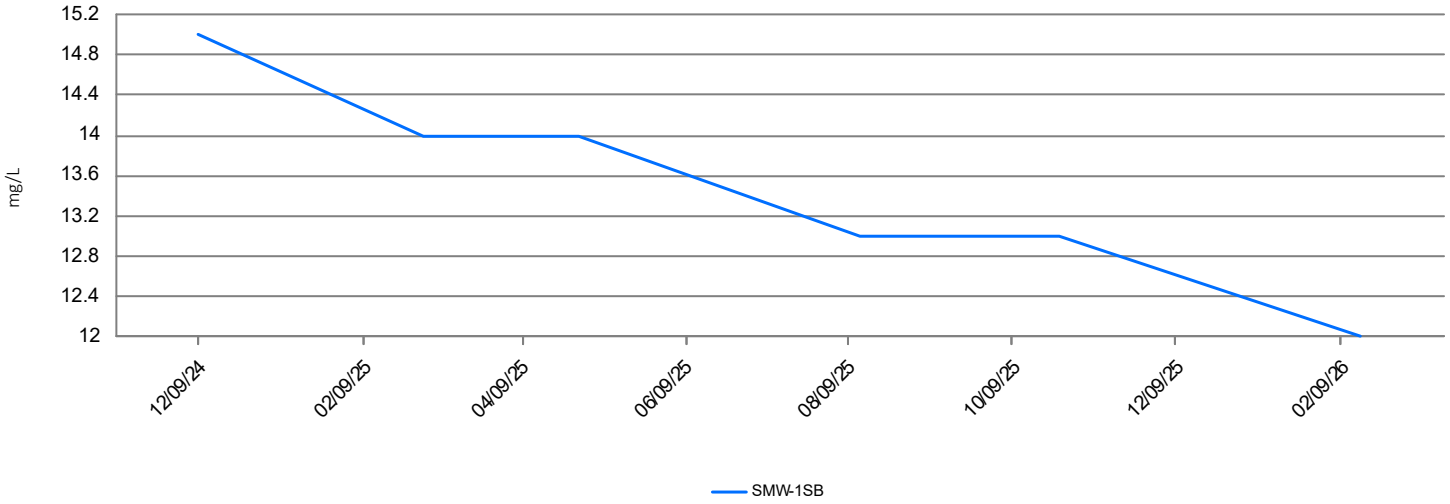
MonitorPro

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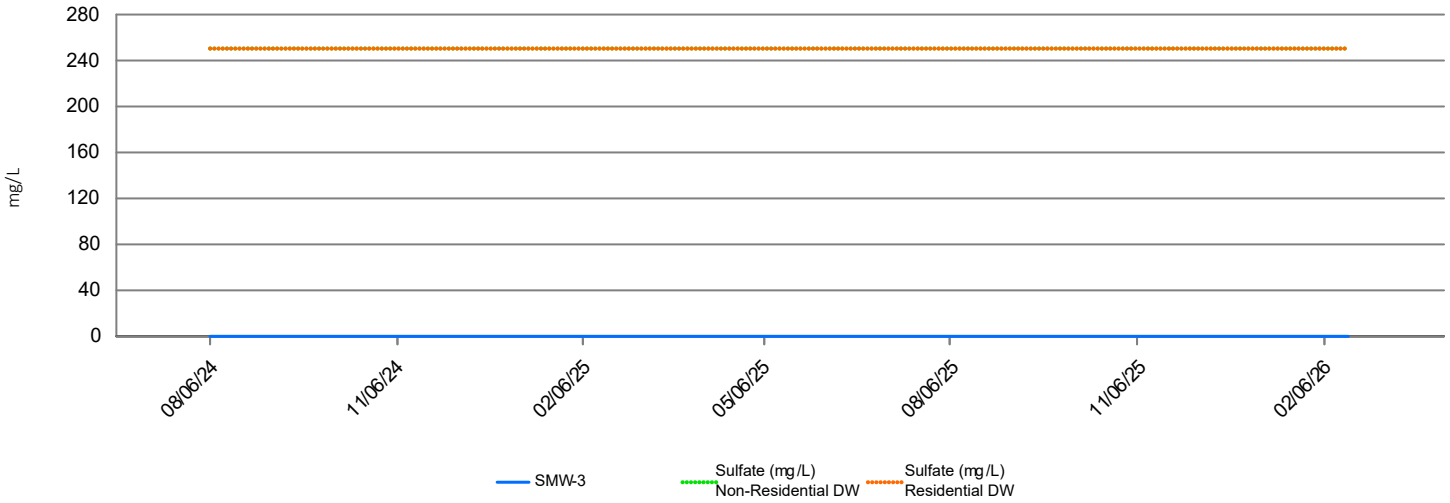
SMW-1



SMW-1SB



SMW-3



Printed Date: 05/21/2026

EHS DATA

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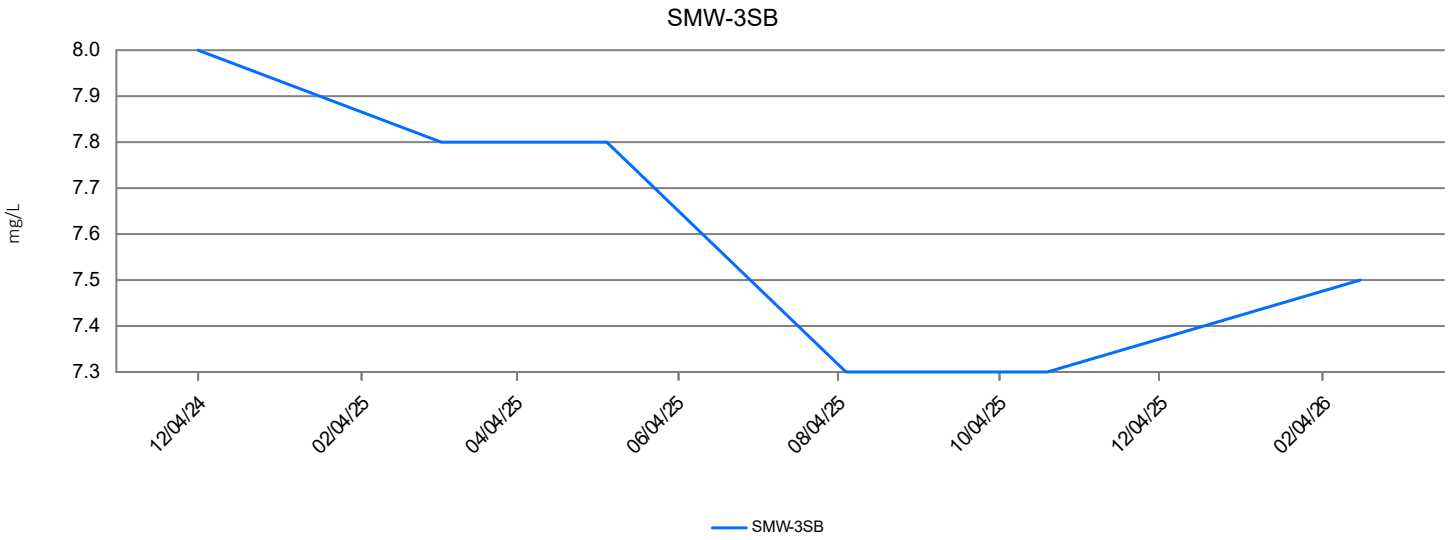
MCERTS

Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sulfate (mg/L)

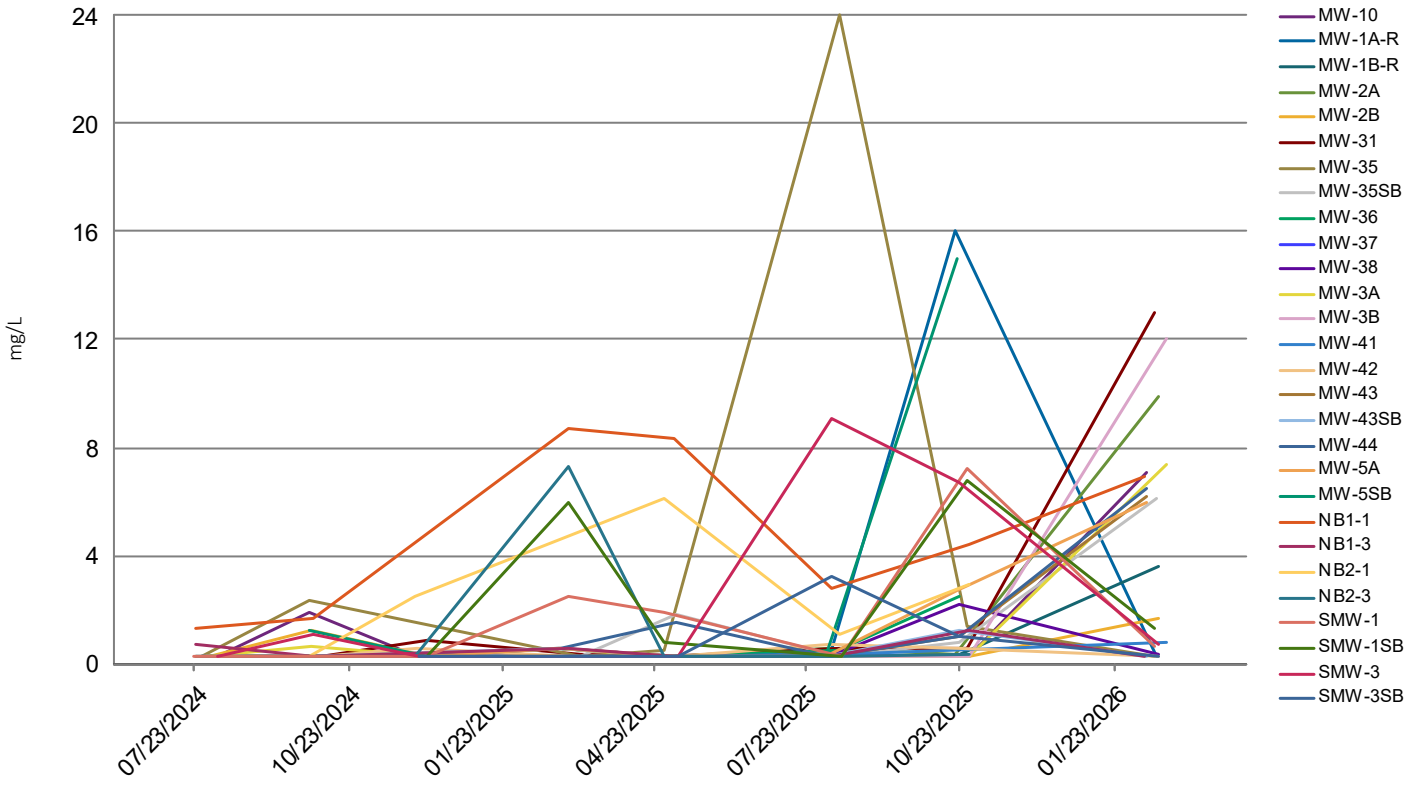


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sulfide (mg/L)



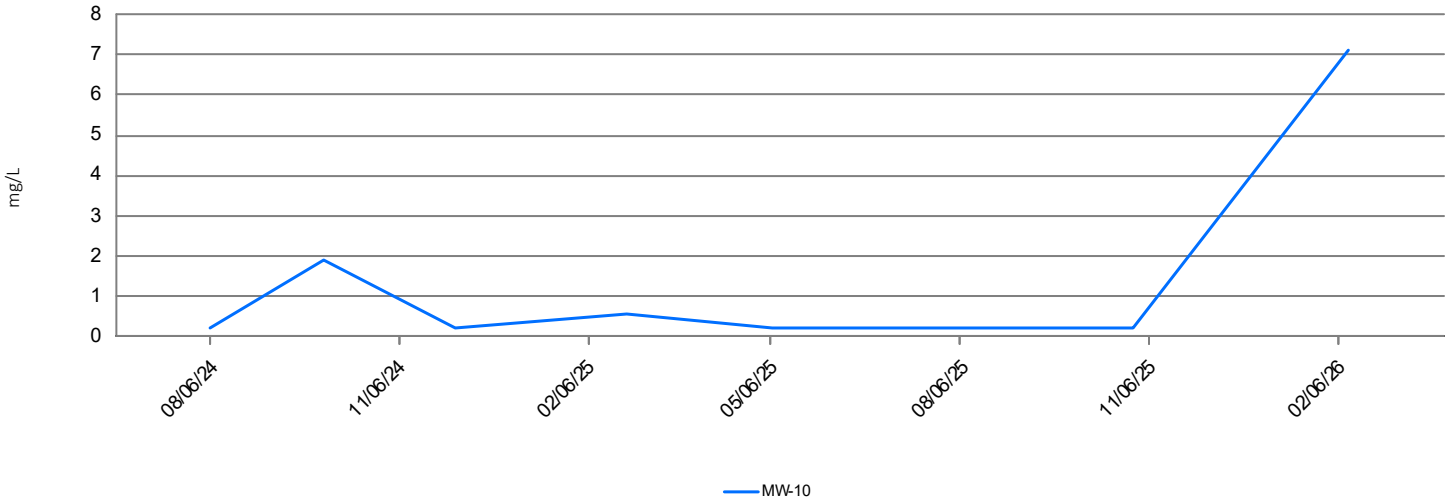
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

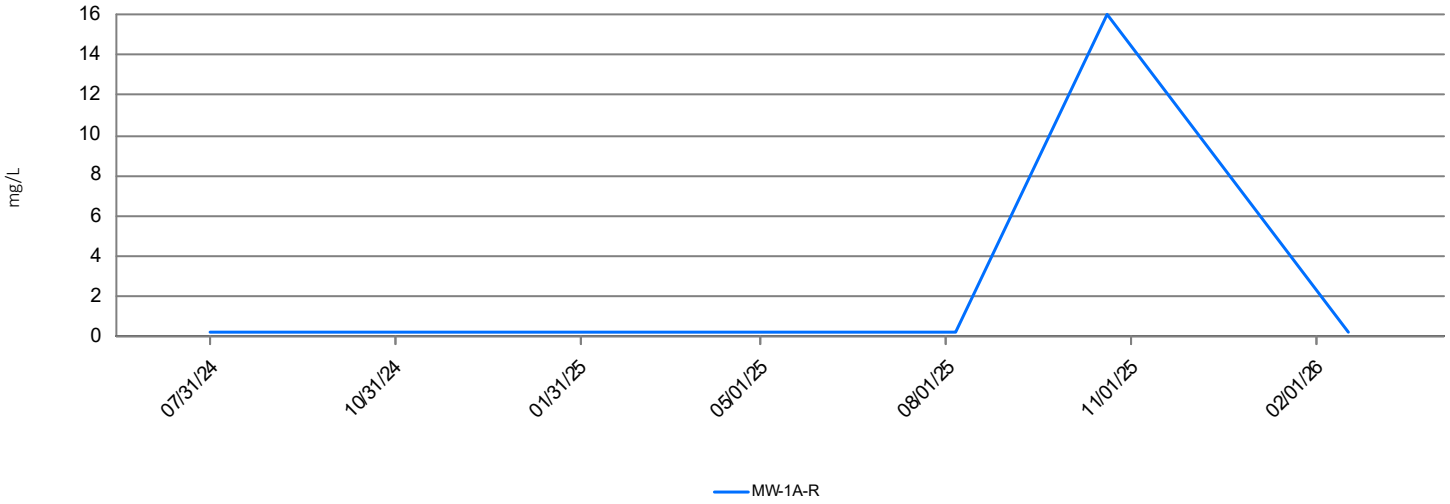
MonitorPro

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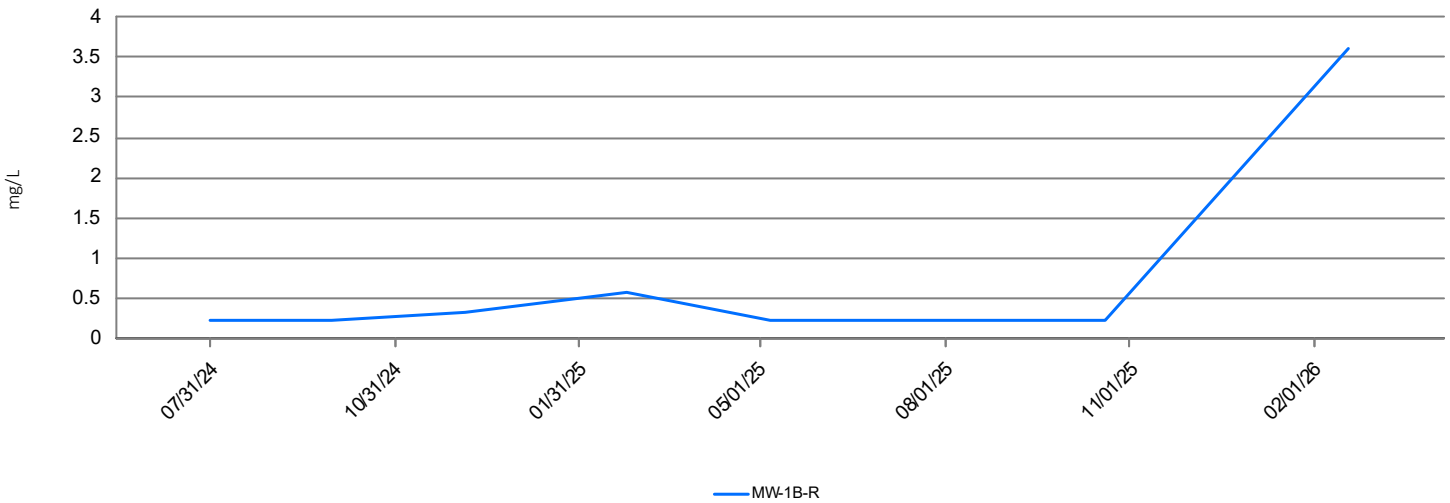
MW-10



MW-1A-R



MW-1B-R



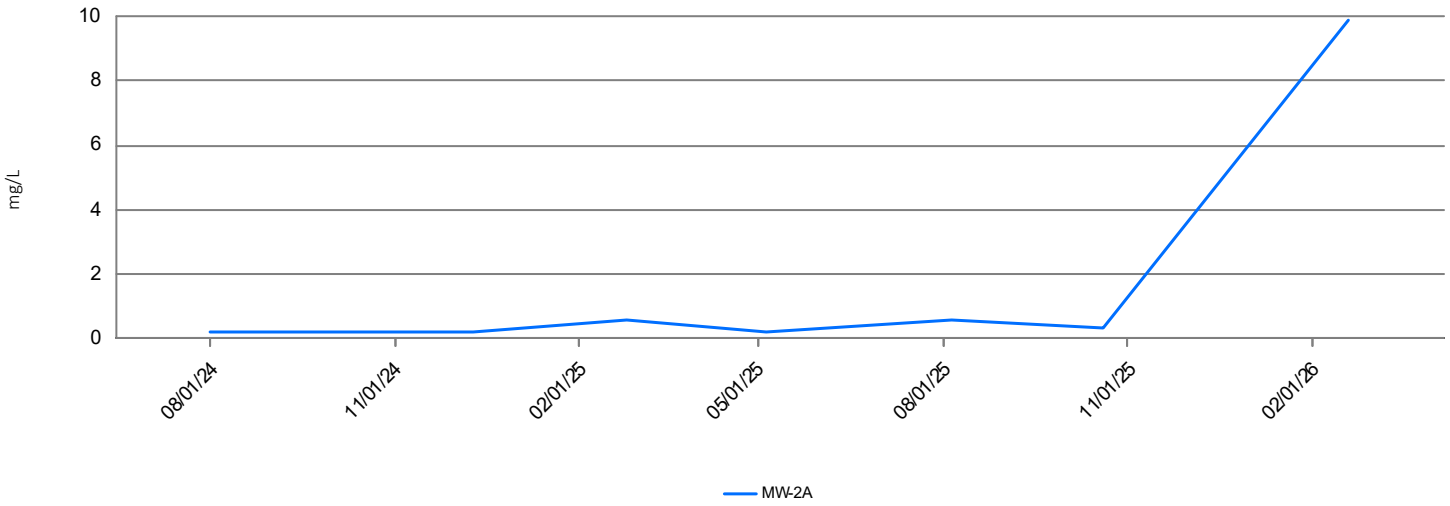
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

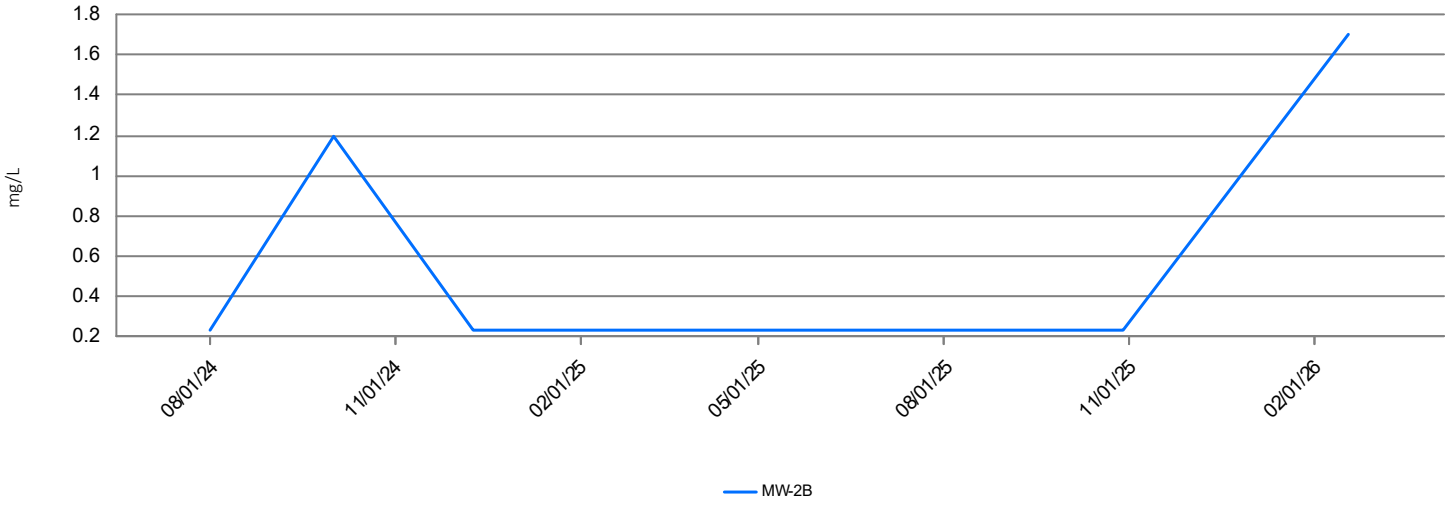
MonitorPro

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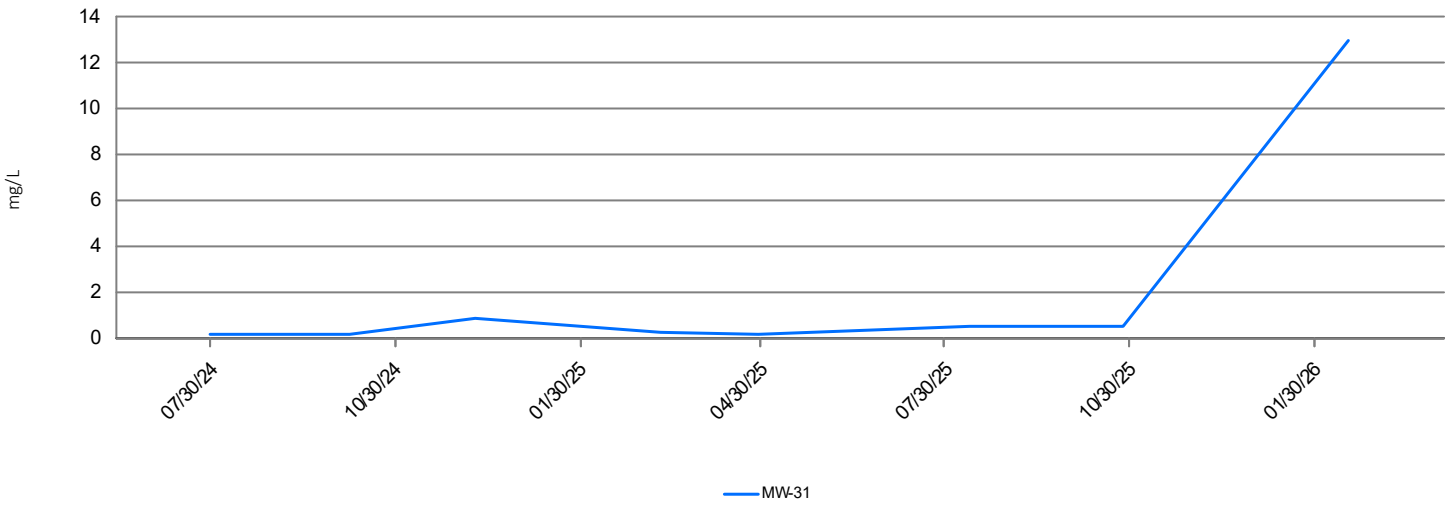
MW-2A



MW-2B



MW-31



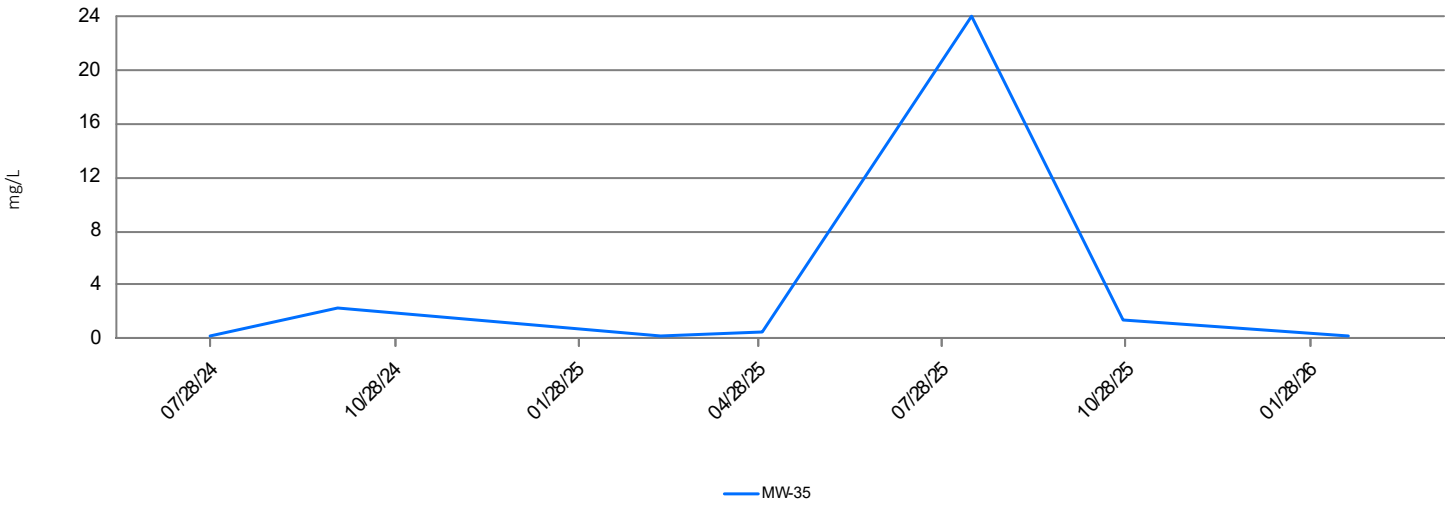
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

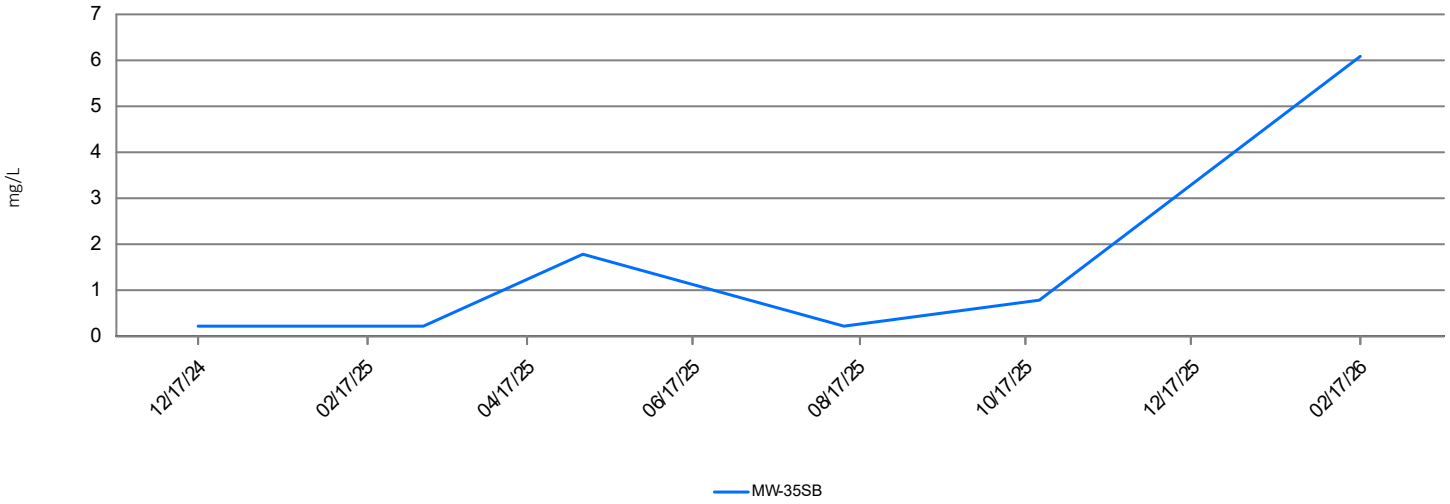
MonitorPro

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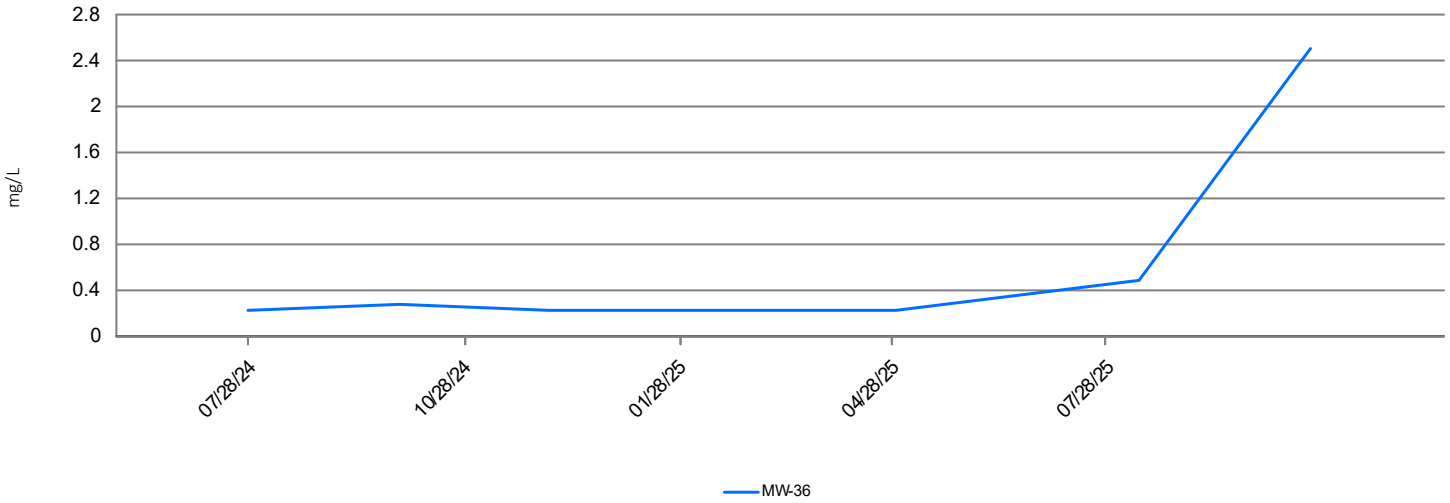
MW-35



MW-35SB



MW-36

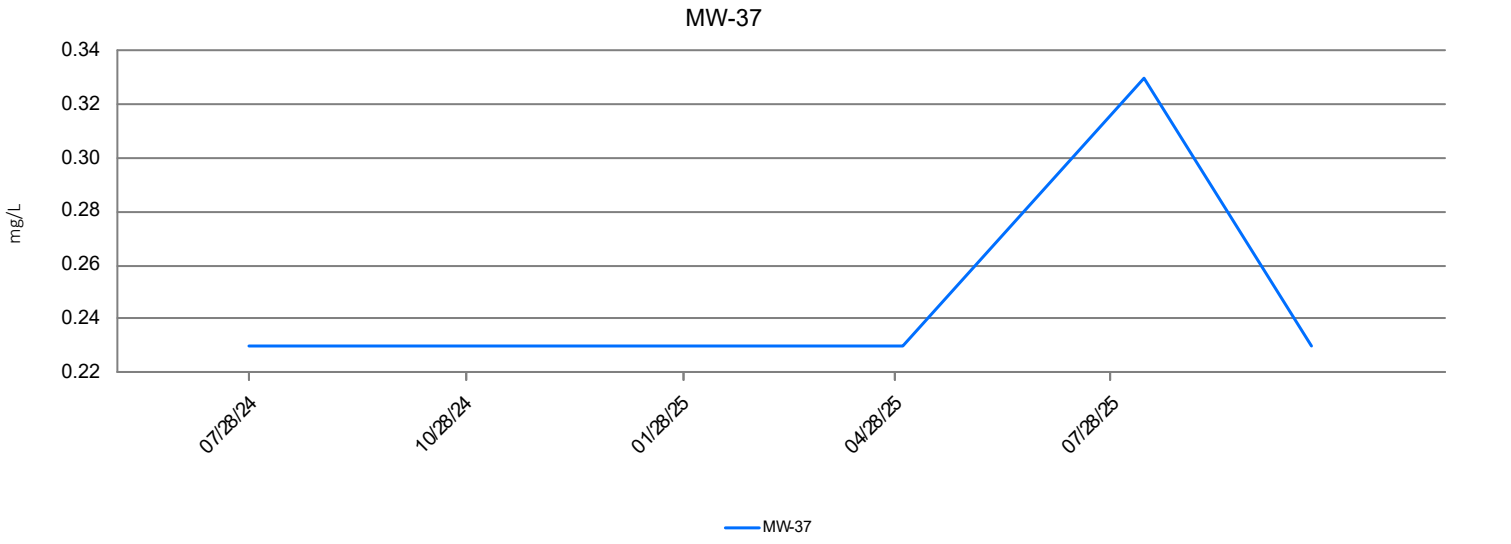


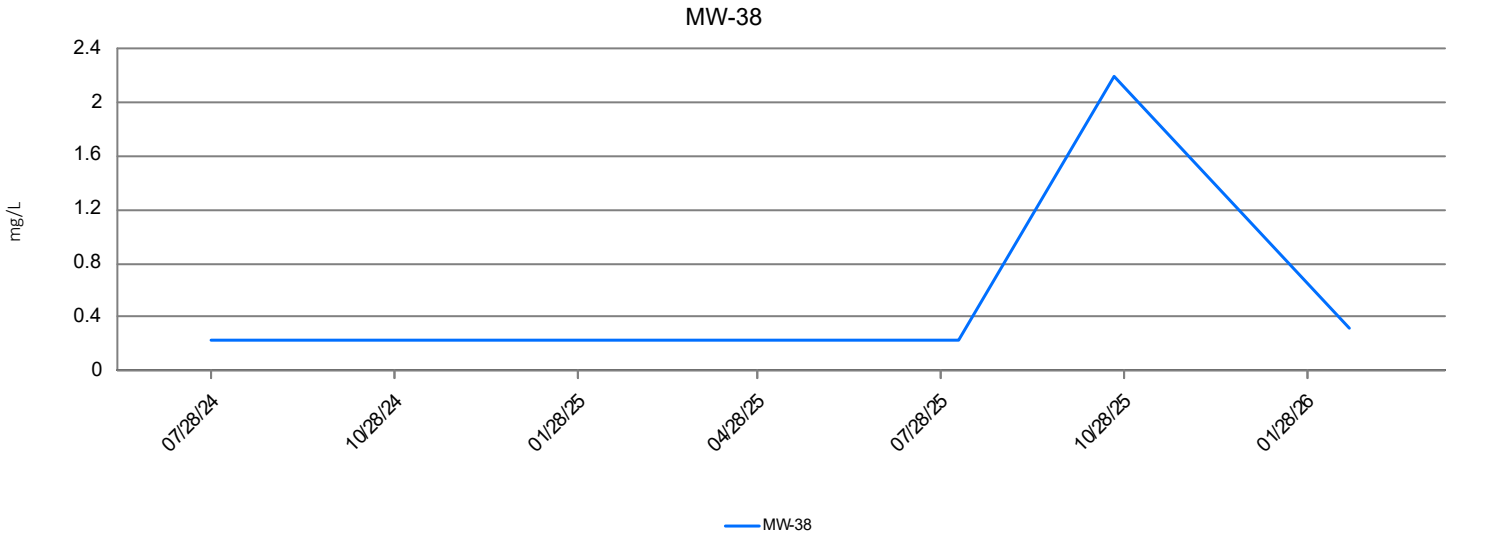
Variable Graphical Report

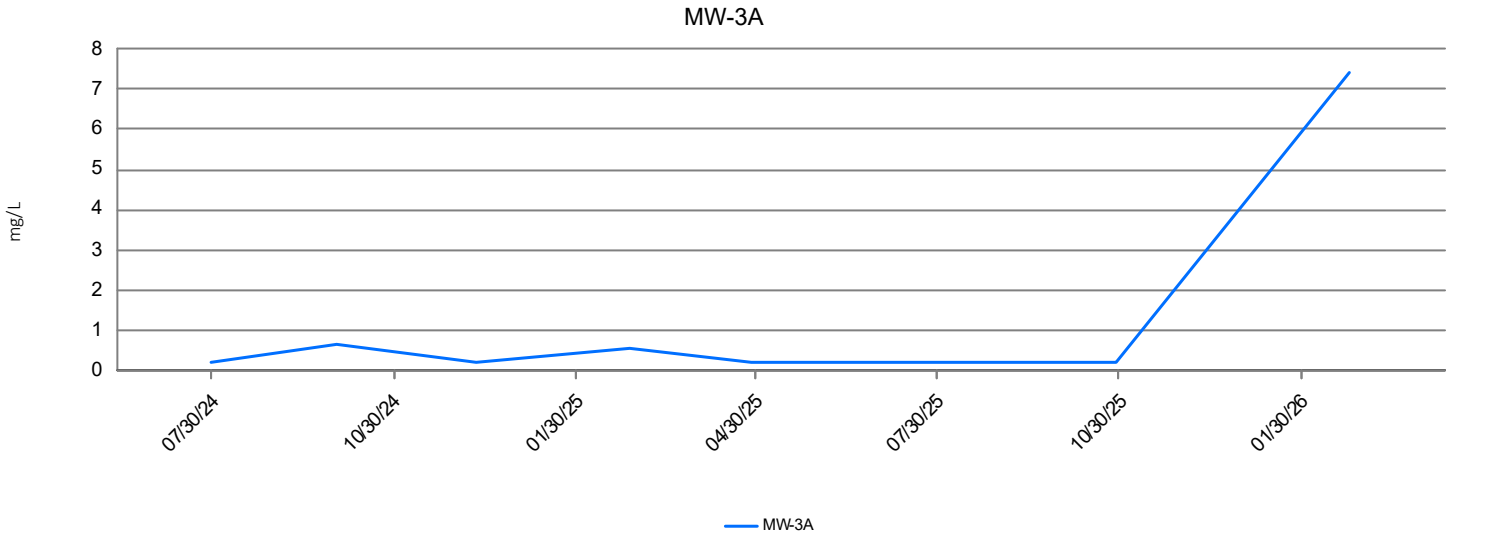
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sulfide (mg/L)







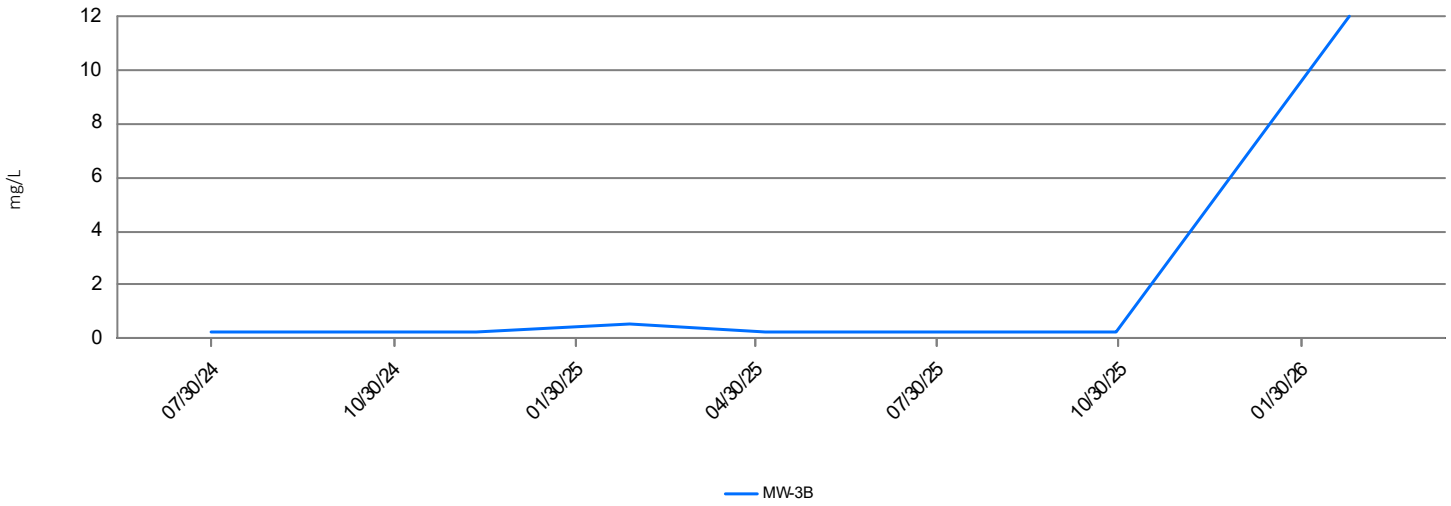
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

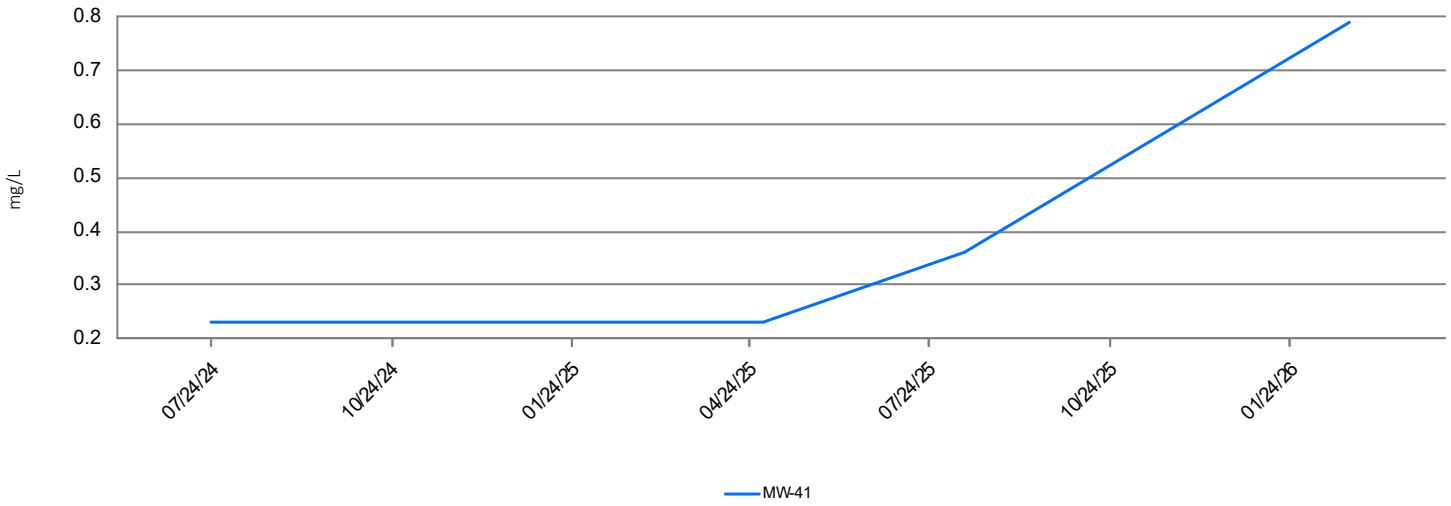
MonitorPro

No Group Selected, Sulfide (mg/L)

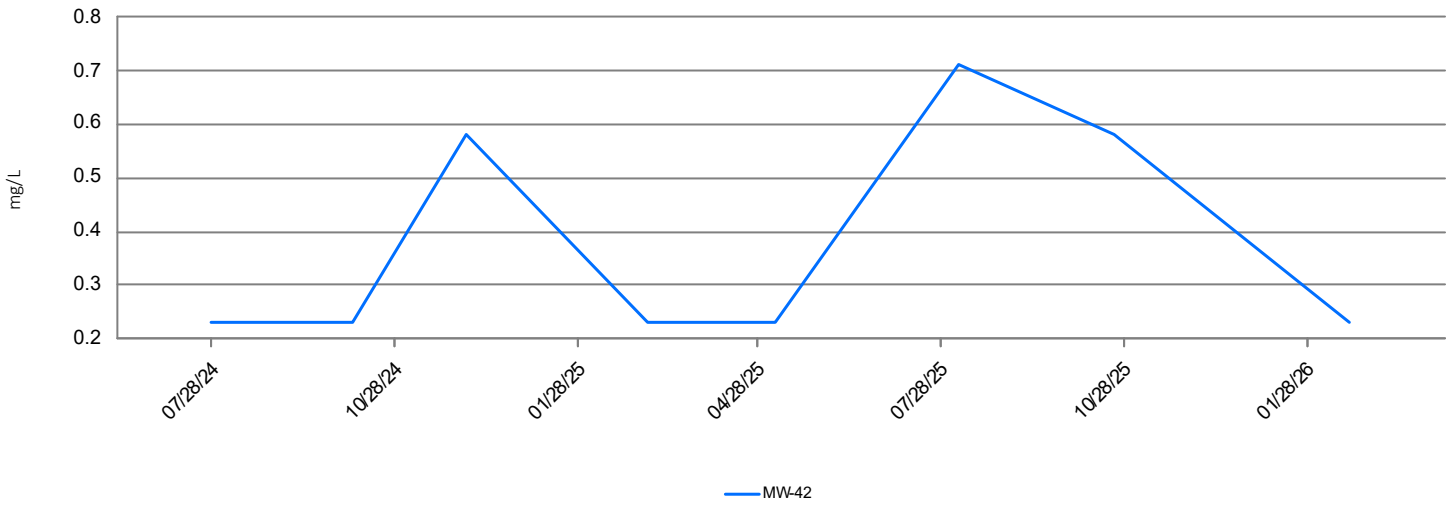
MW-3B



MW-41



MW-42



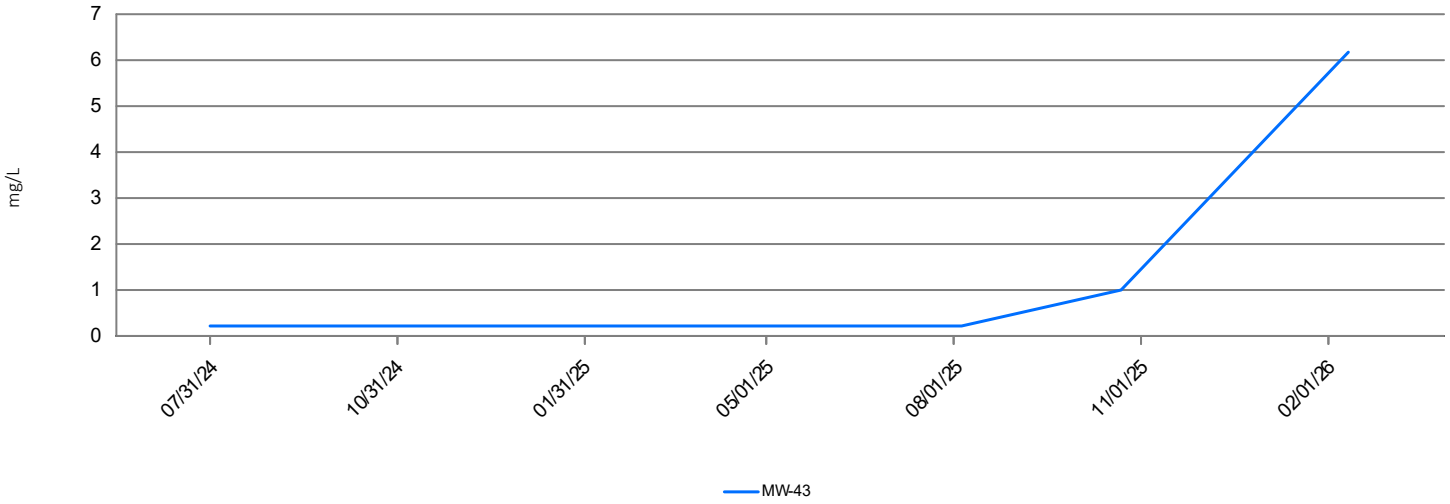
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

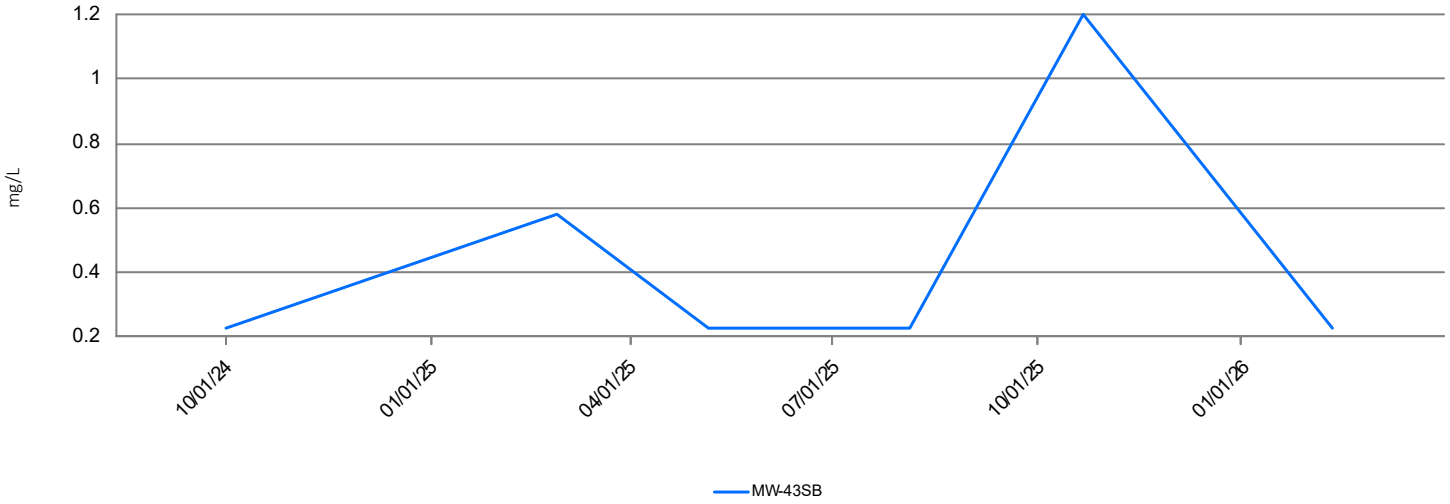
MonitorPro

No Group Selected, Sulfide (mg/L)

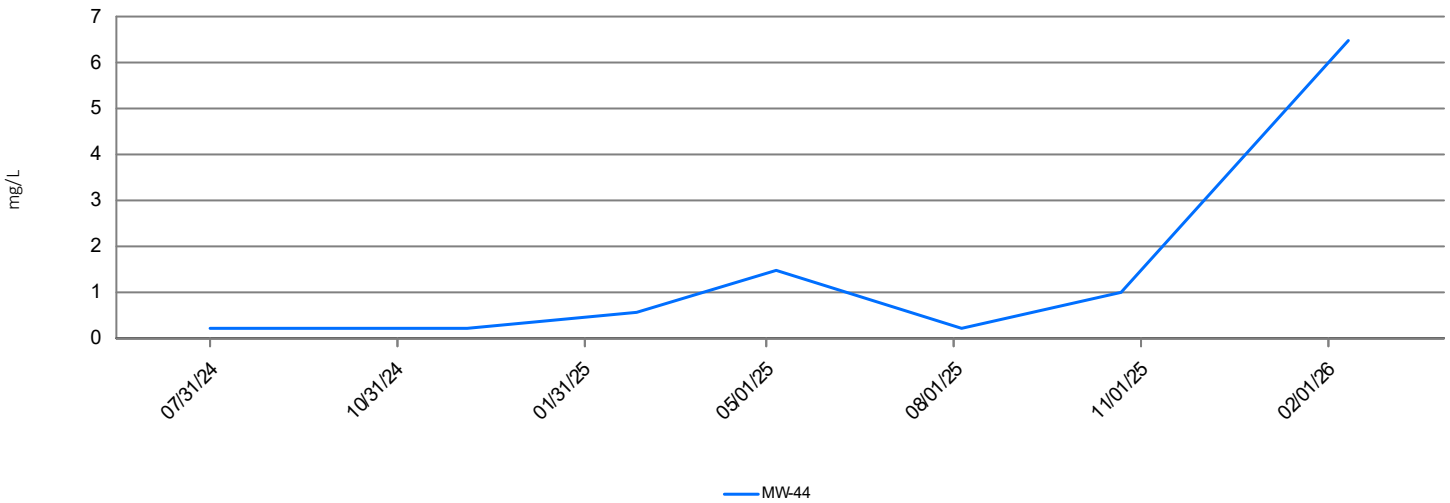
MW-43



MW-43SB



MW-44



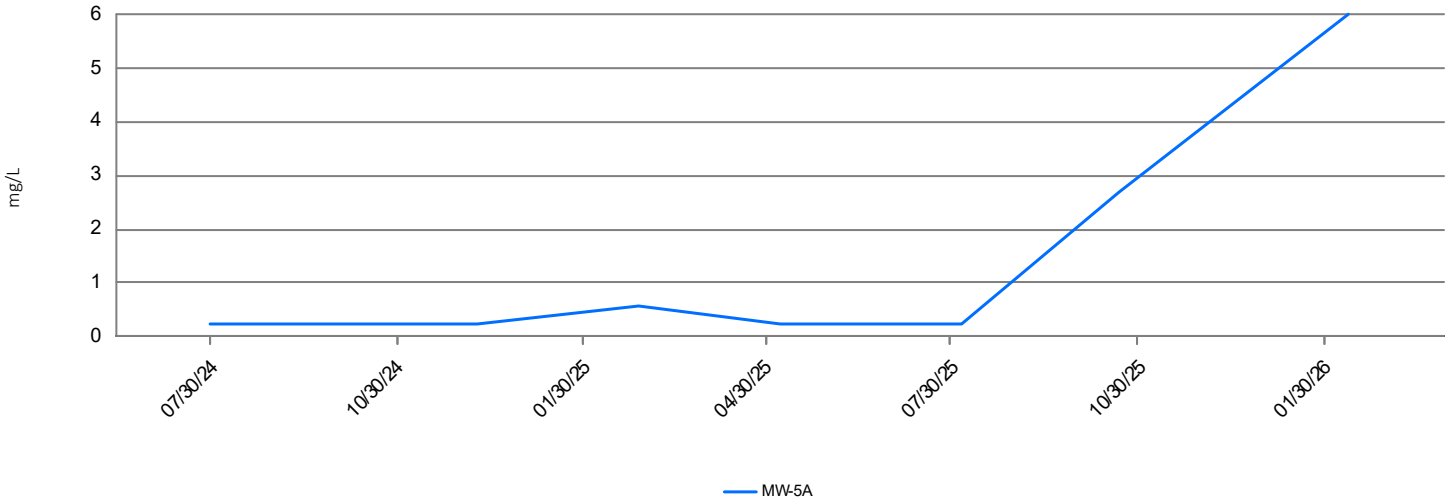
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

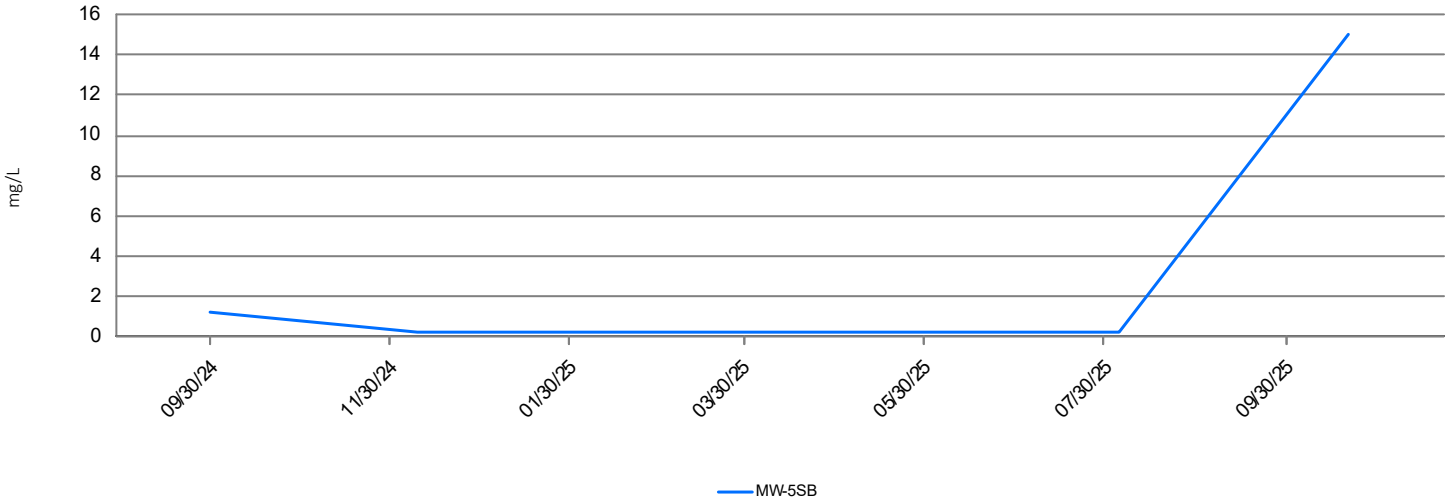
MonitorPro

No Group Selected, Sulfide (mg/L)

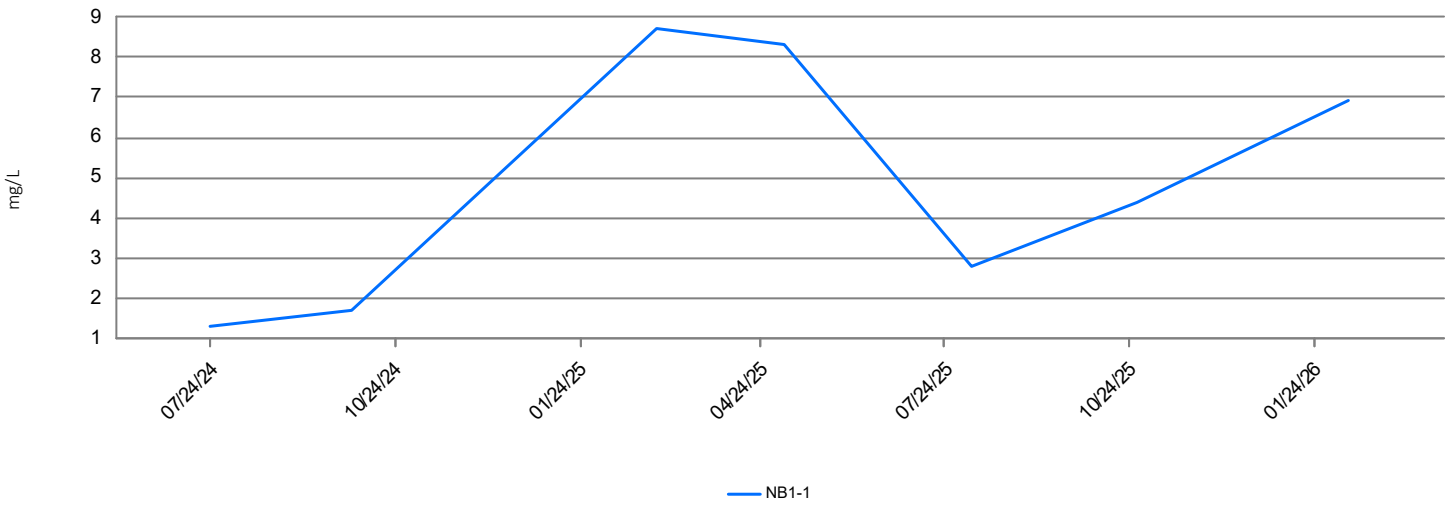
MW-5A



MW-5SB



NB1-1



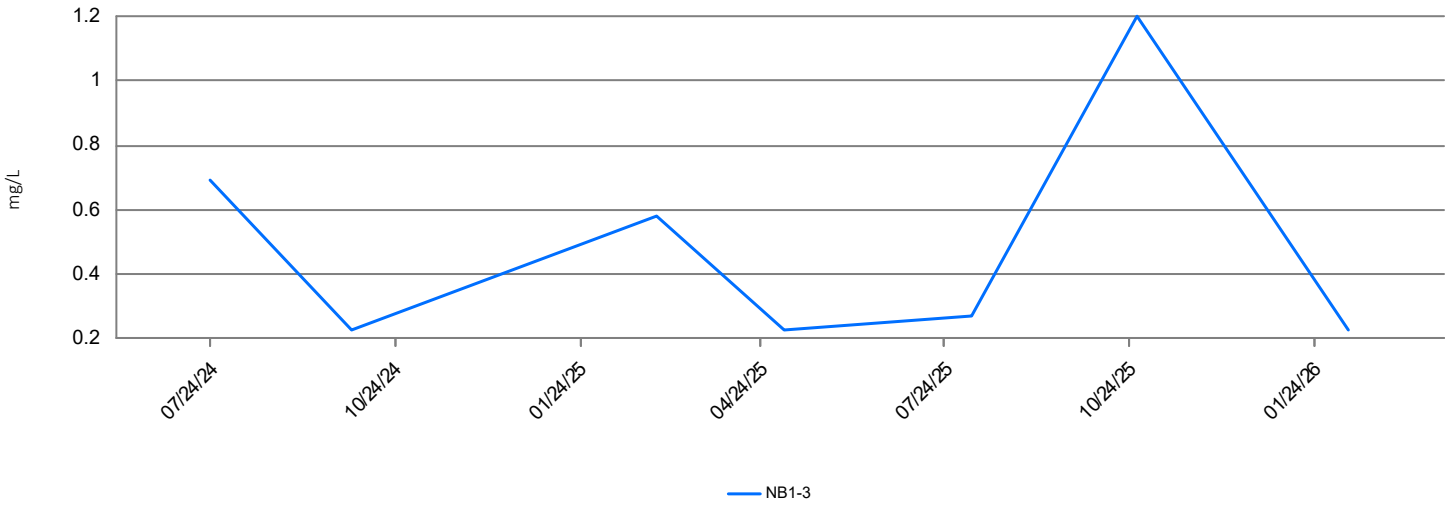
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

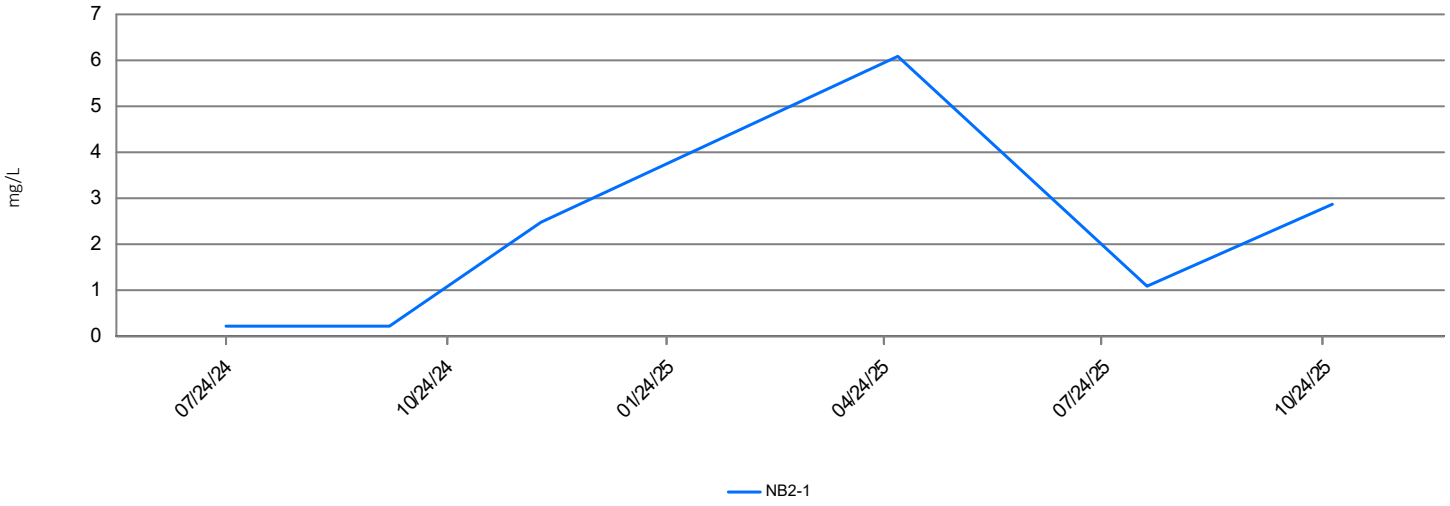
MonitorPro

No Group Selected, Sulfide (mg/L)

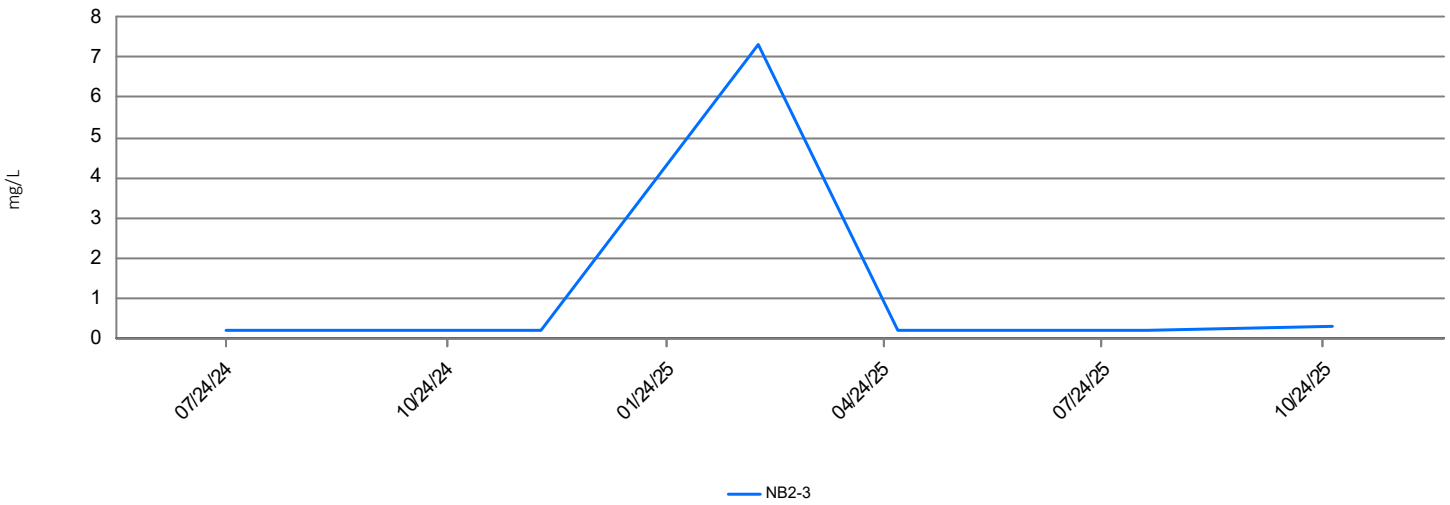
NB1-3



NB2-1



NB2-3



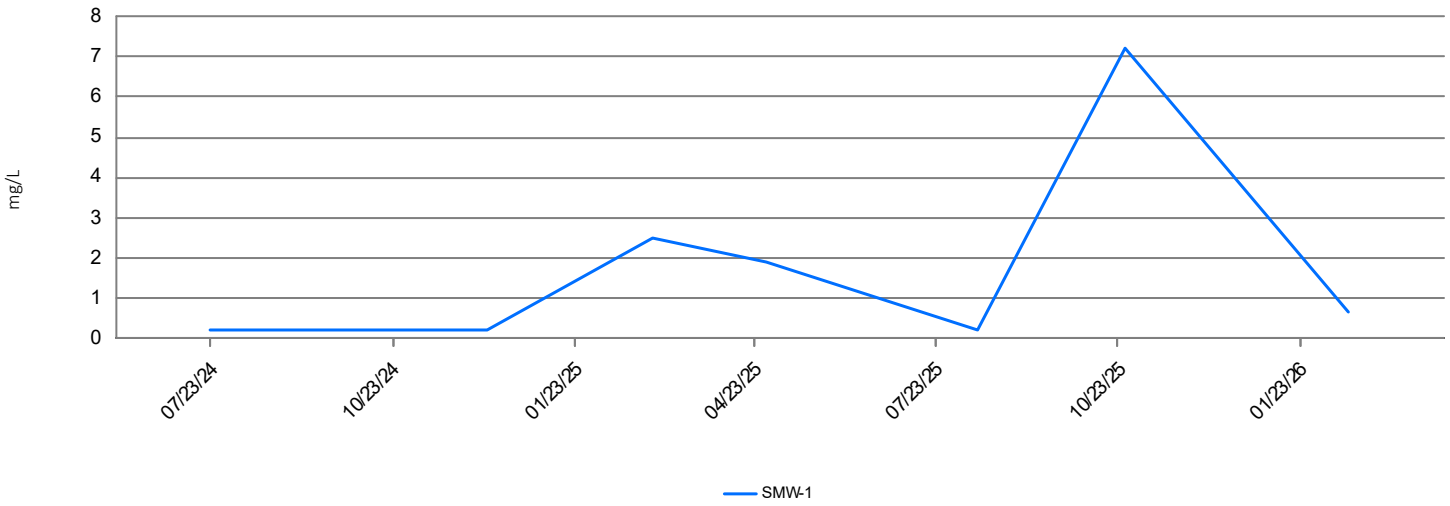
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

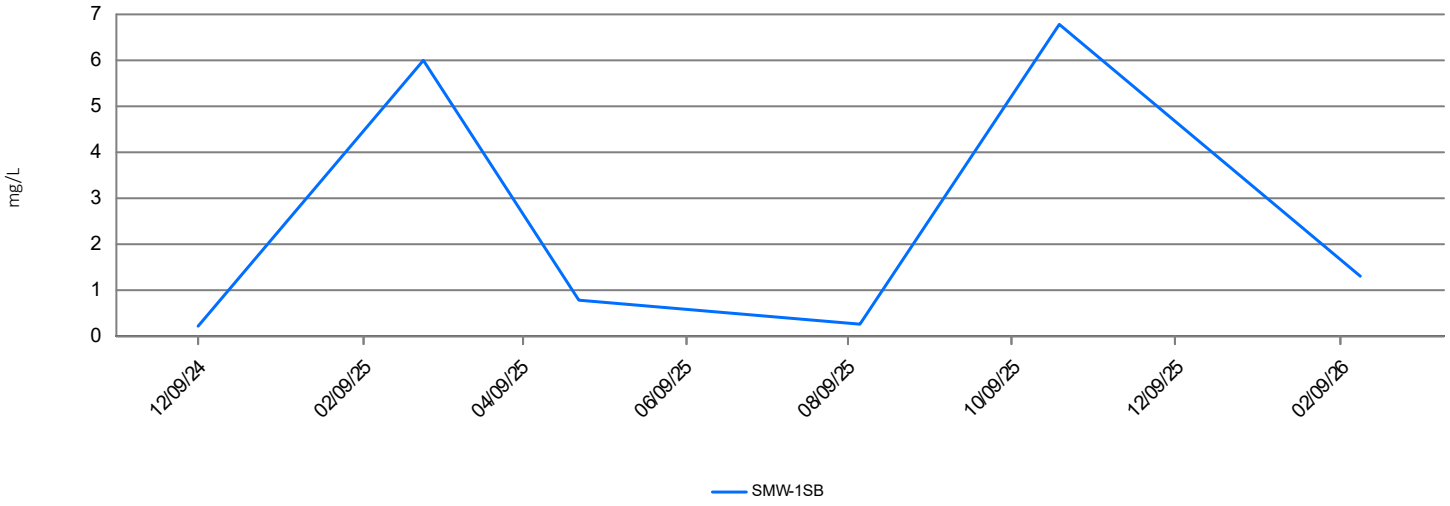
MonitorPro

No Group Selected, Sulfide (mg/L)

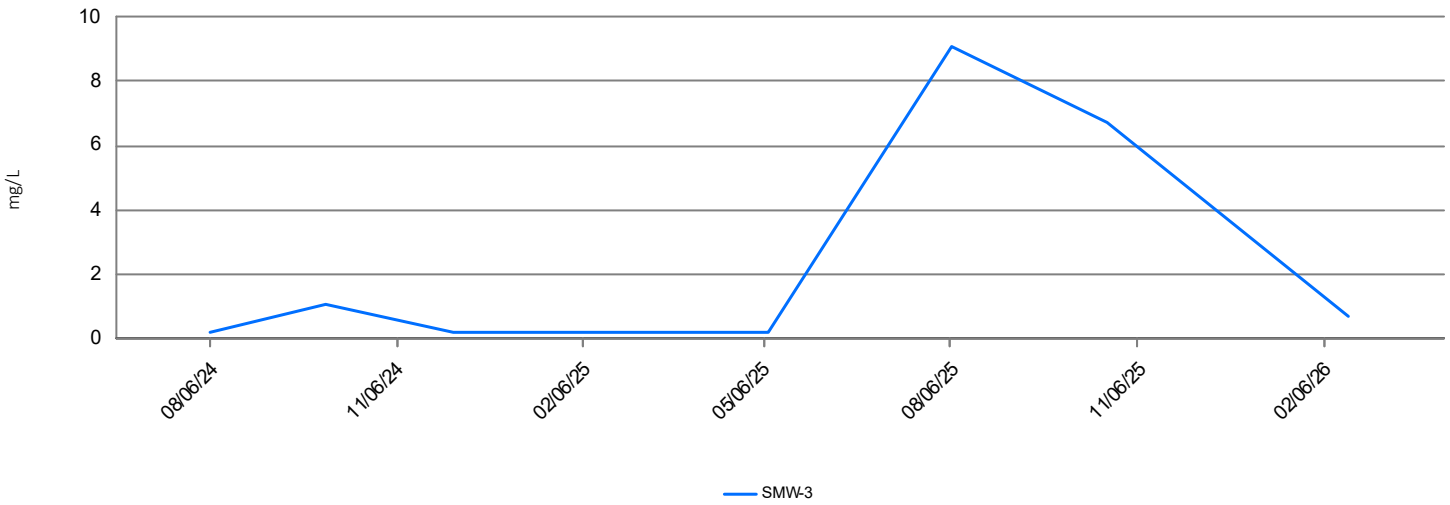
SMW-1



SMW-1SB



SMW-3

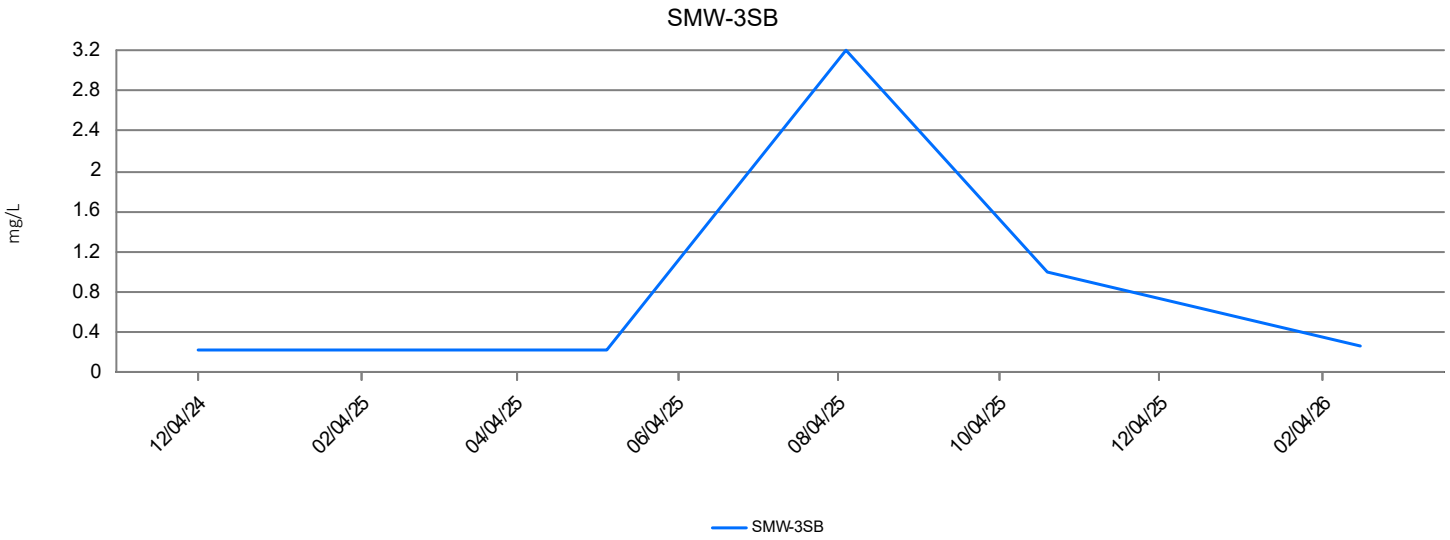


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Sulfide (mg/L)

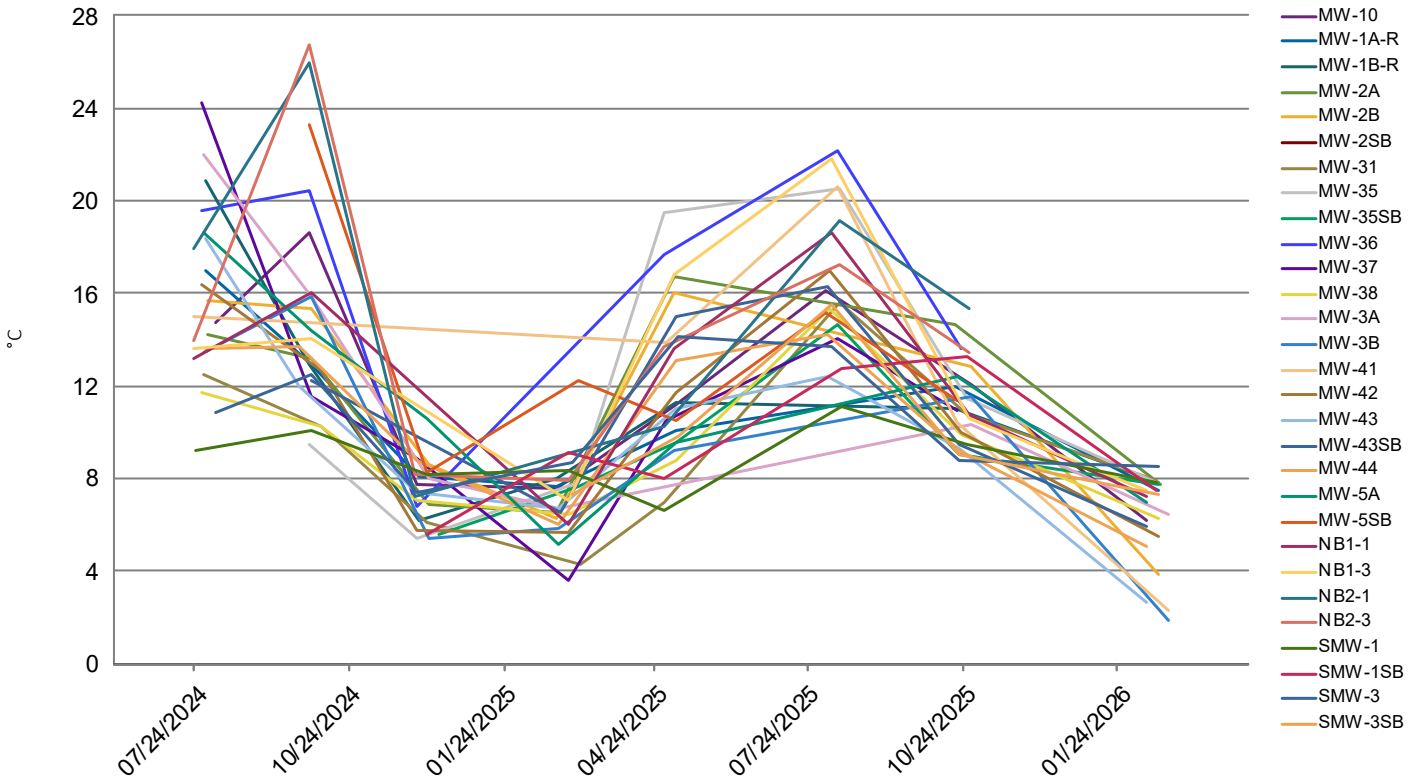


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Temperature Field (°C)



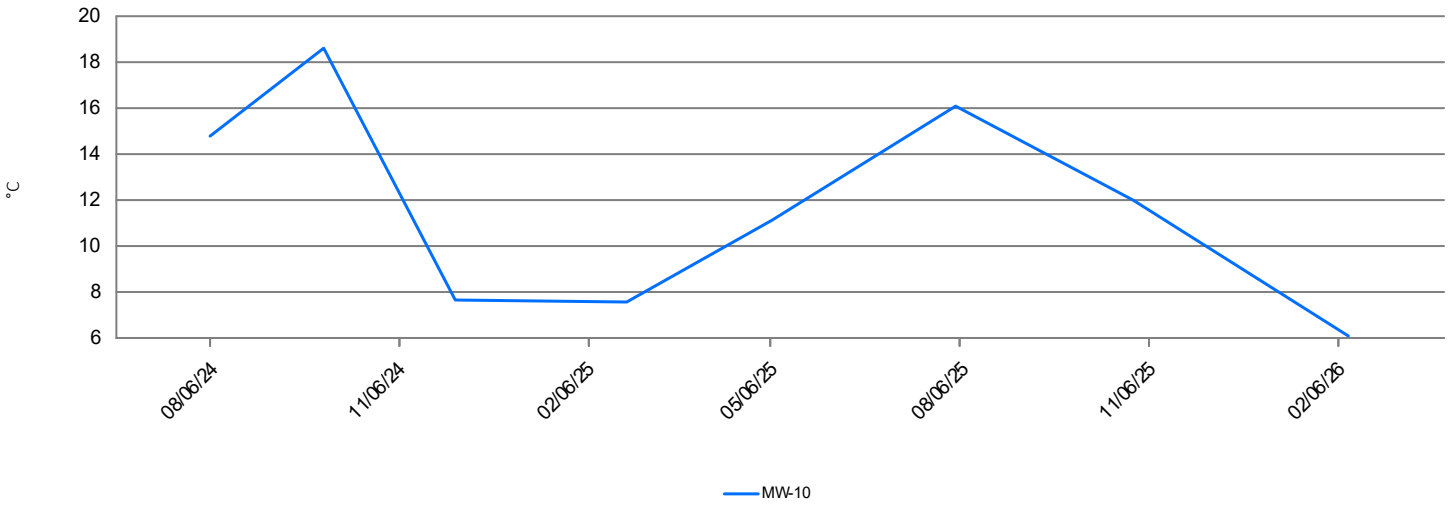
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

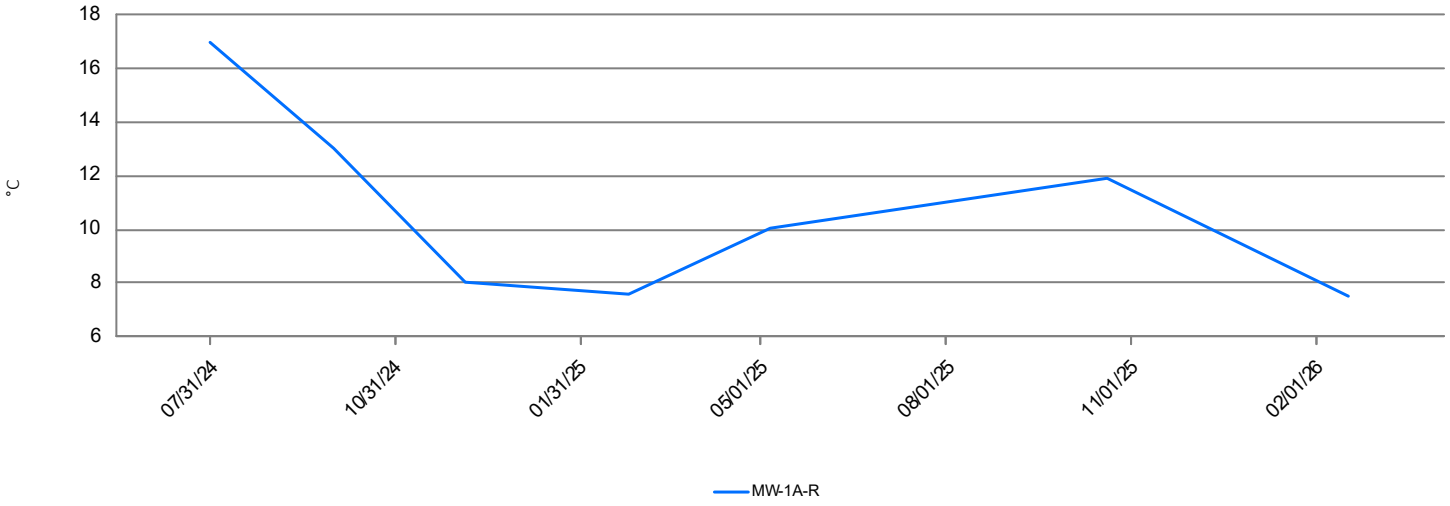
MonitorPro

No Group Selected, Temperature Field (°C)

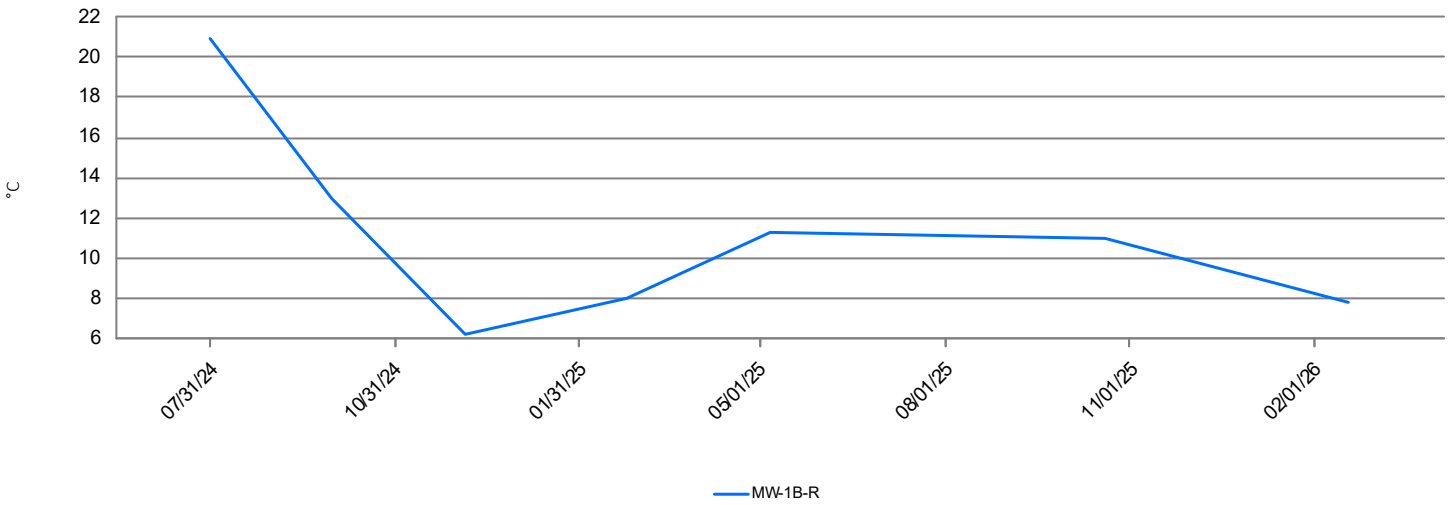
MW-10



MW-1A-R



MW-1B-R

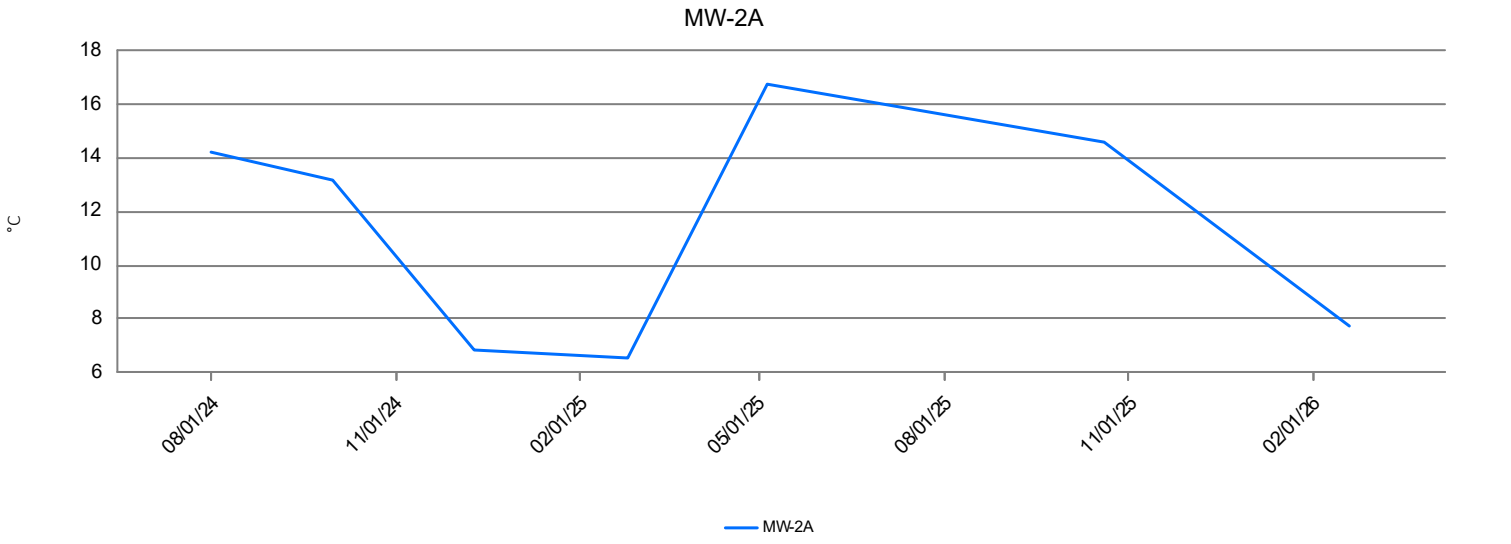


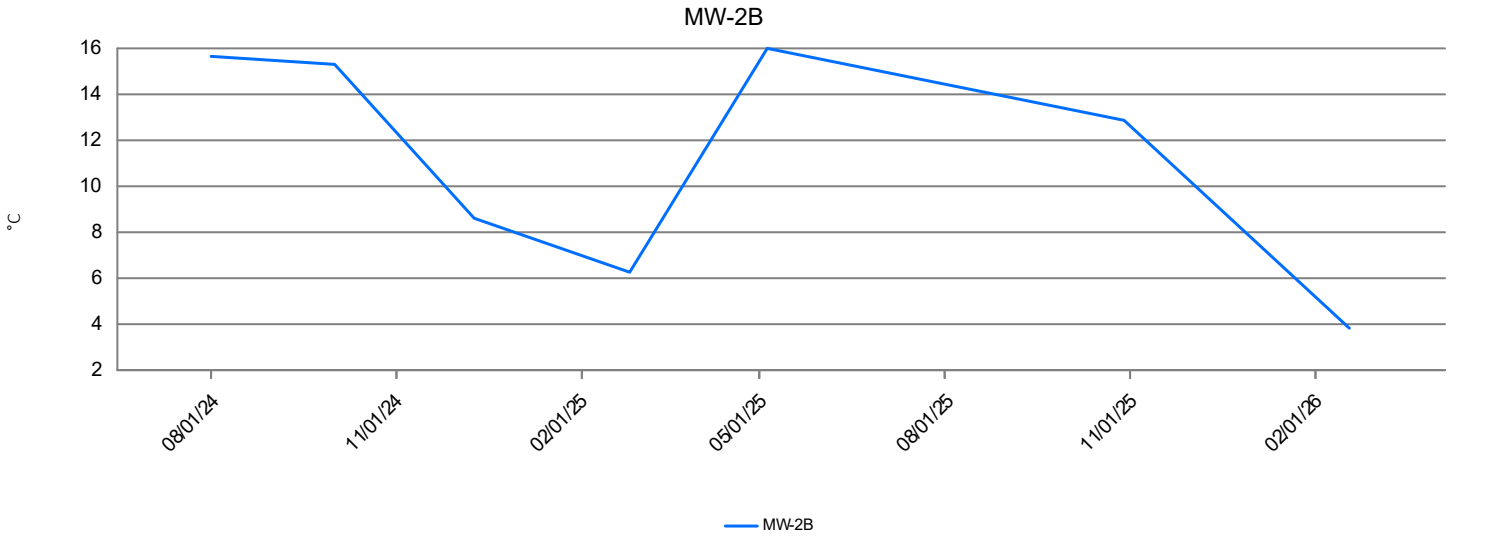
Variable Graphical Report

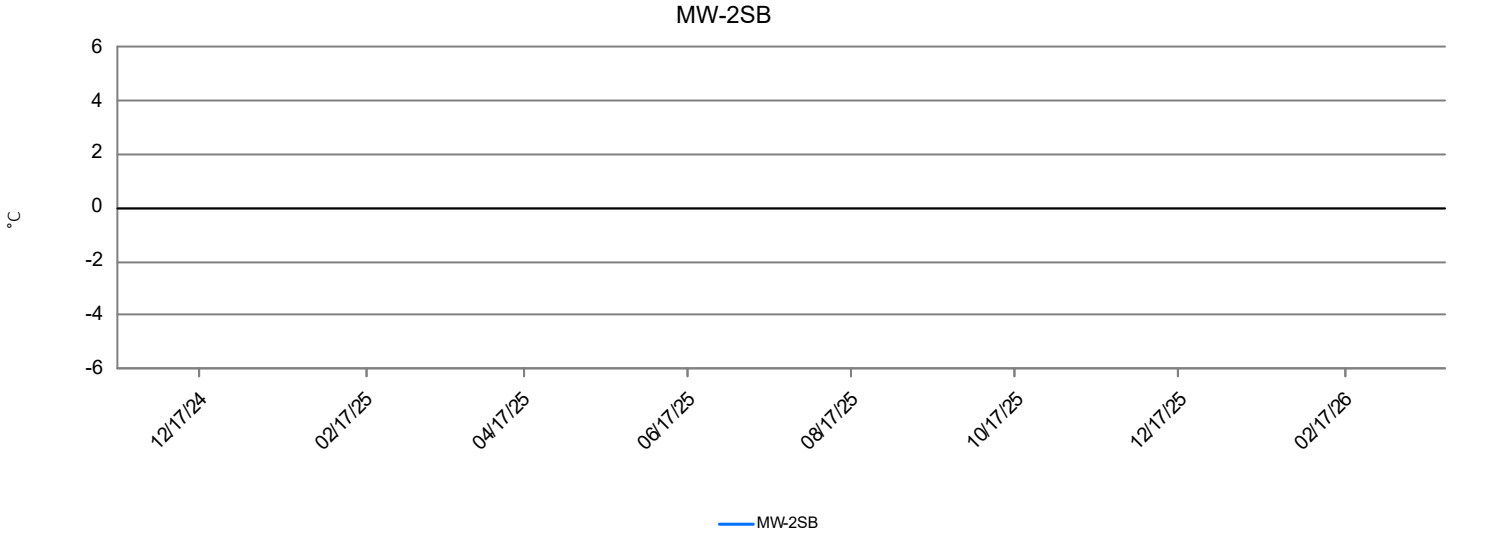
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Temperature Field (°C)





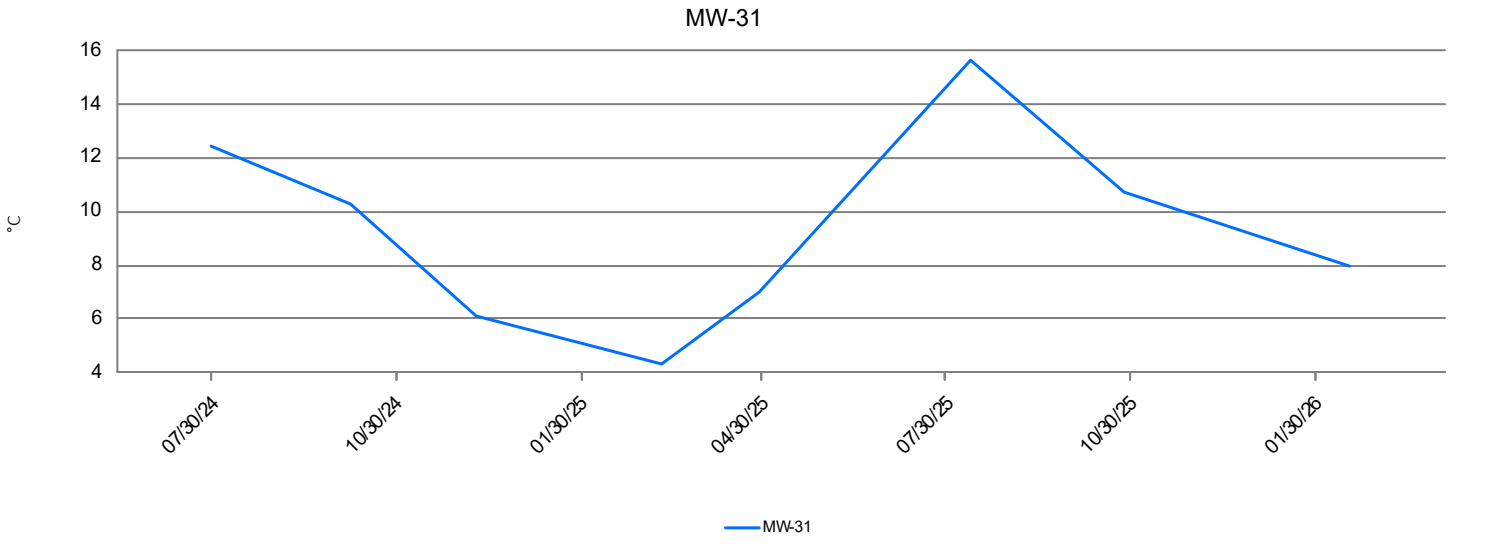


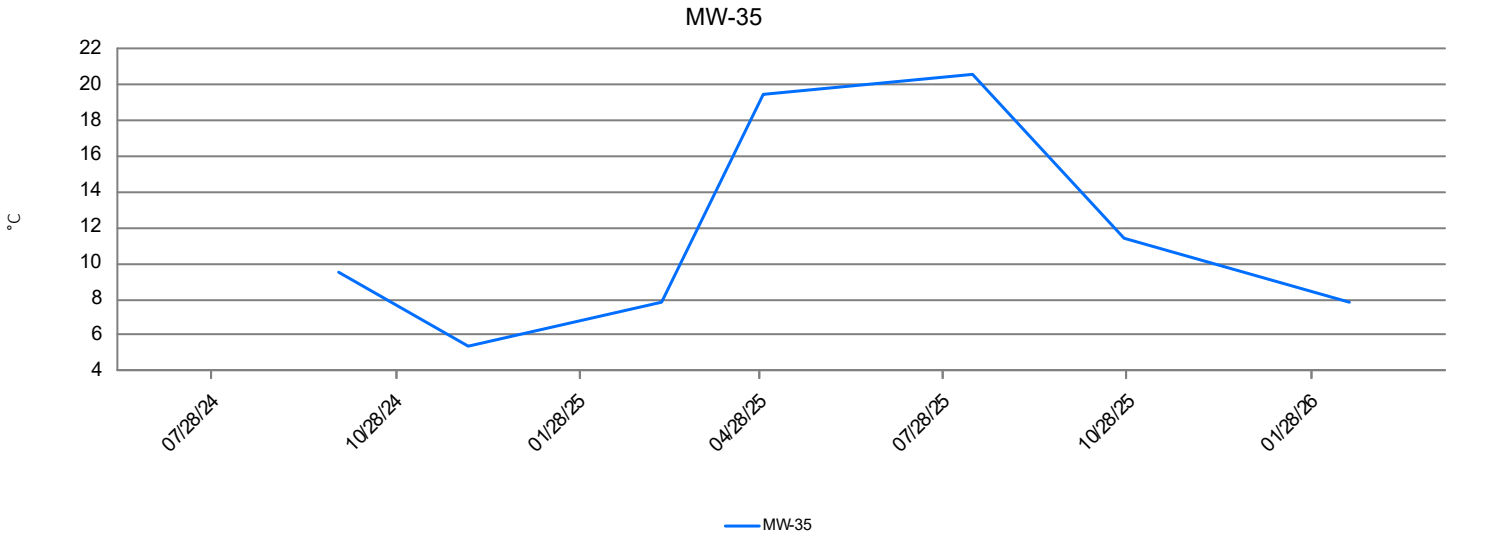
Variable Graphical Report

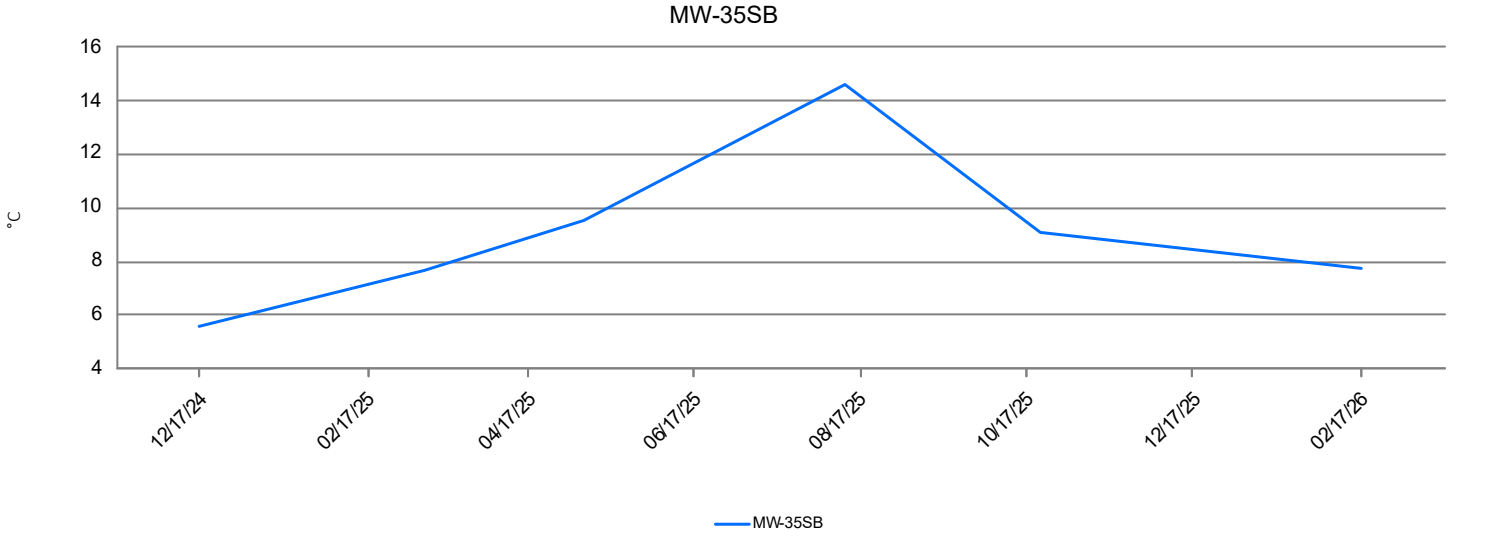
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Temperature Field (°C)







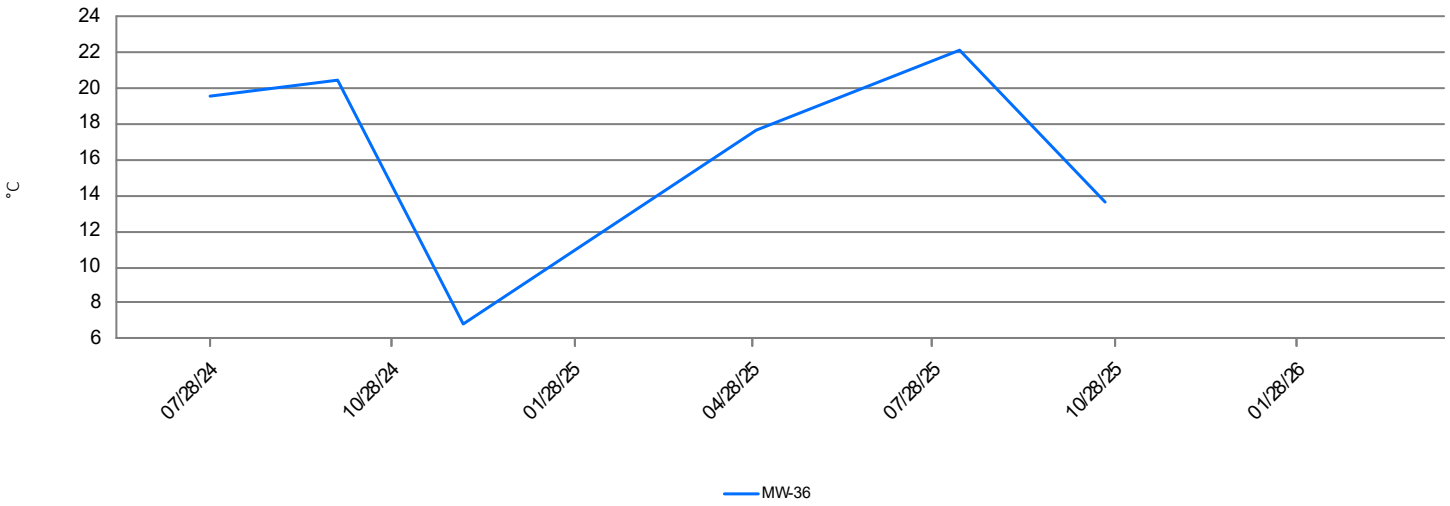
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

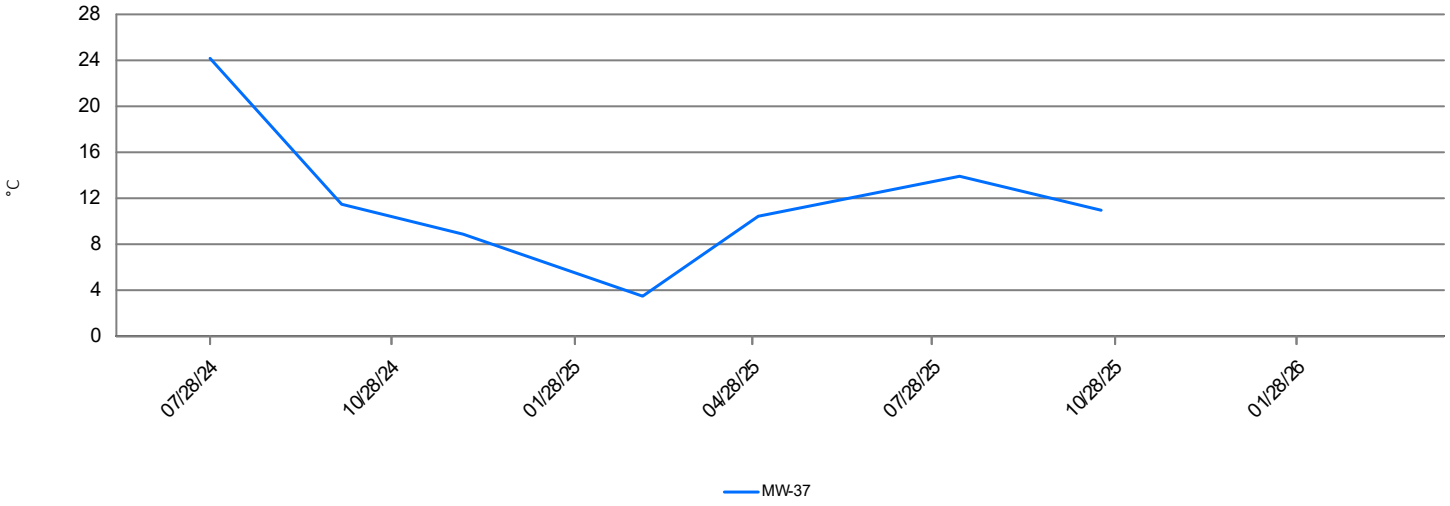
MonitorPro

No Group Selected, Temperature Field (°C)

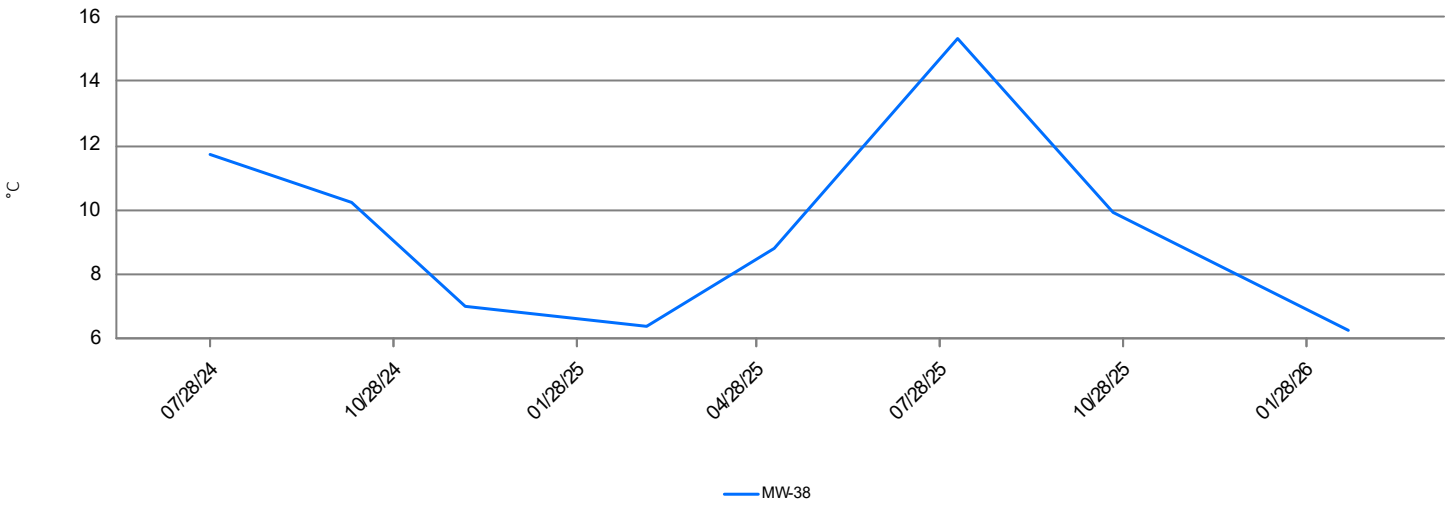
MW-36



MW-37



MW-38



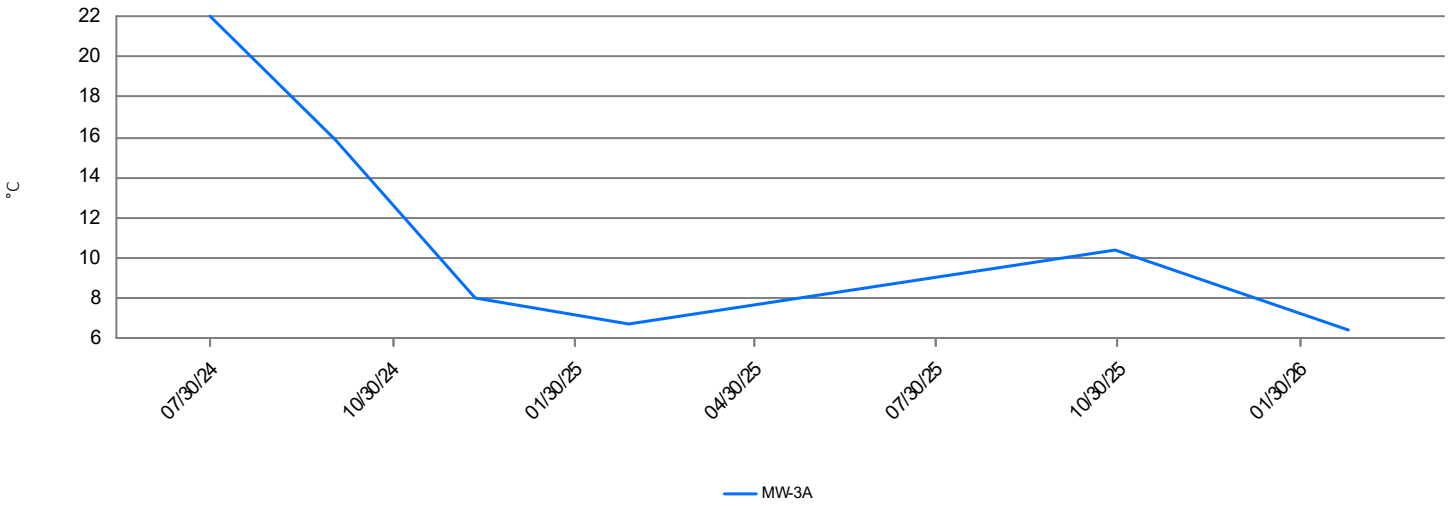
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

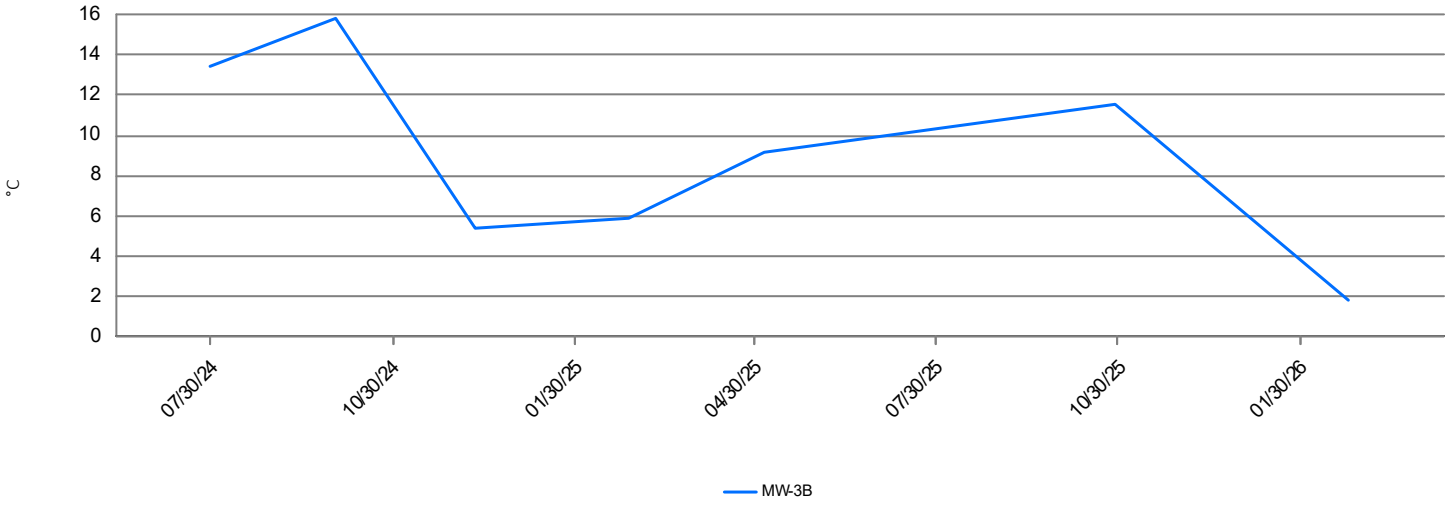
MonitorPro

No Group Selected, Temperature Field (°C)

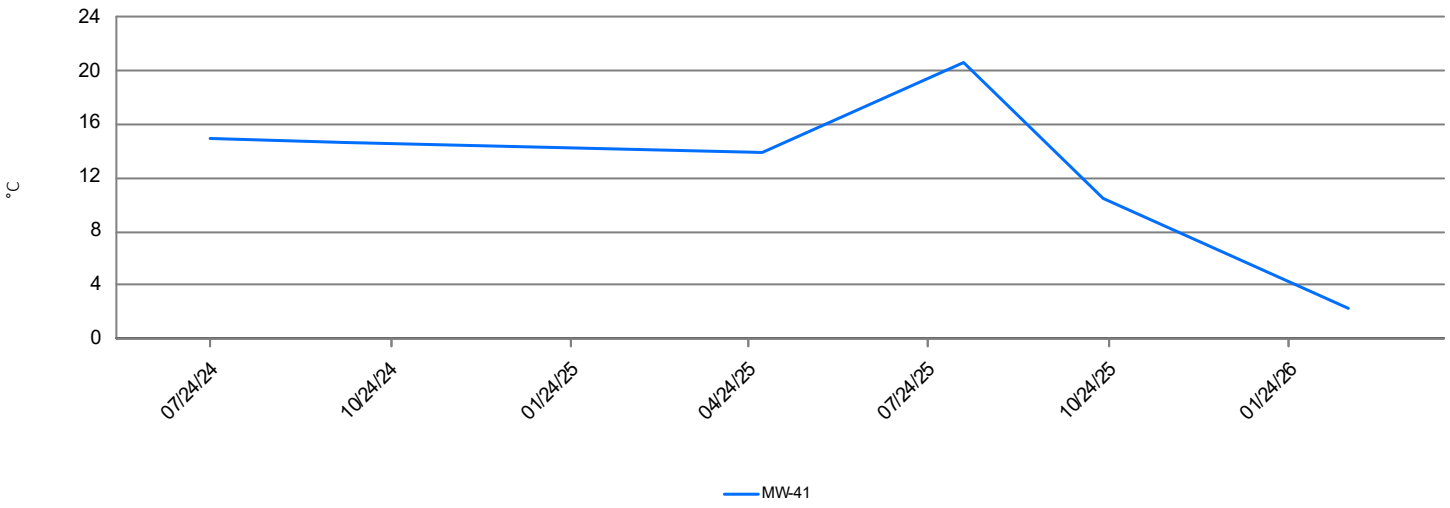
MW-3A



MW-3B



MW-41



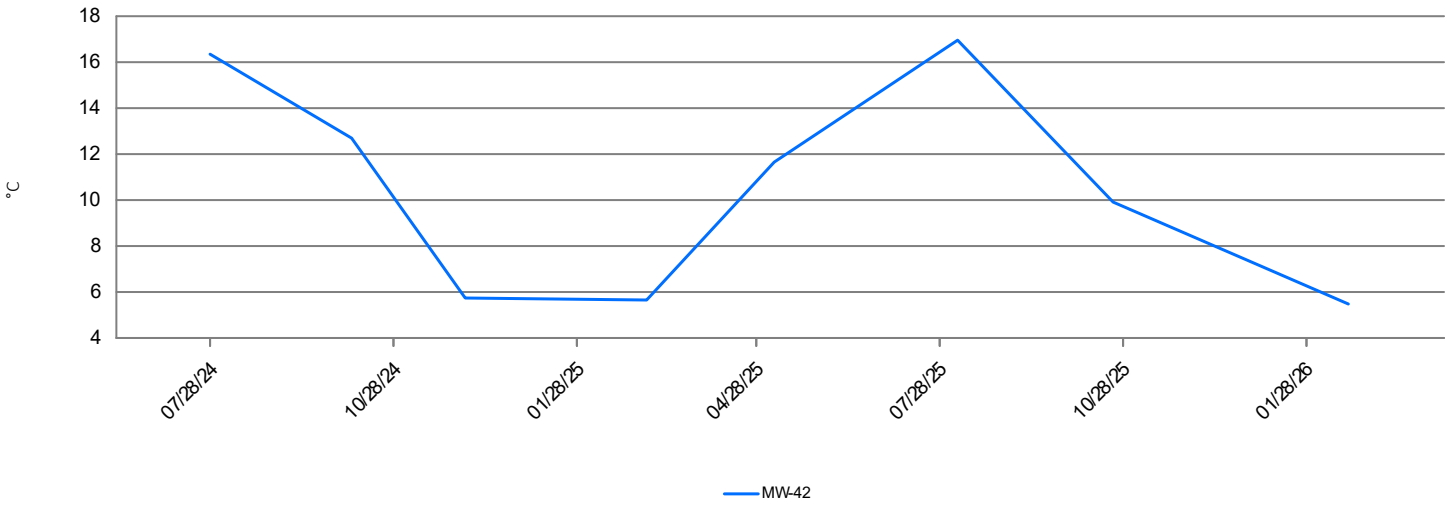
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

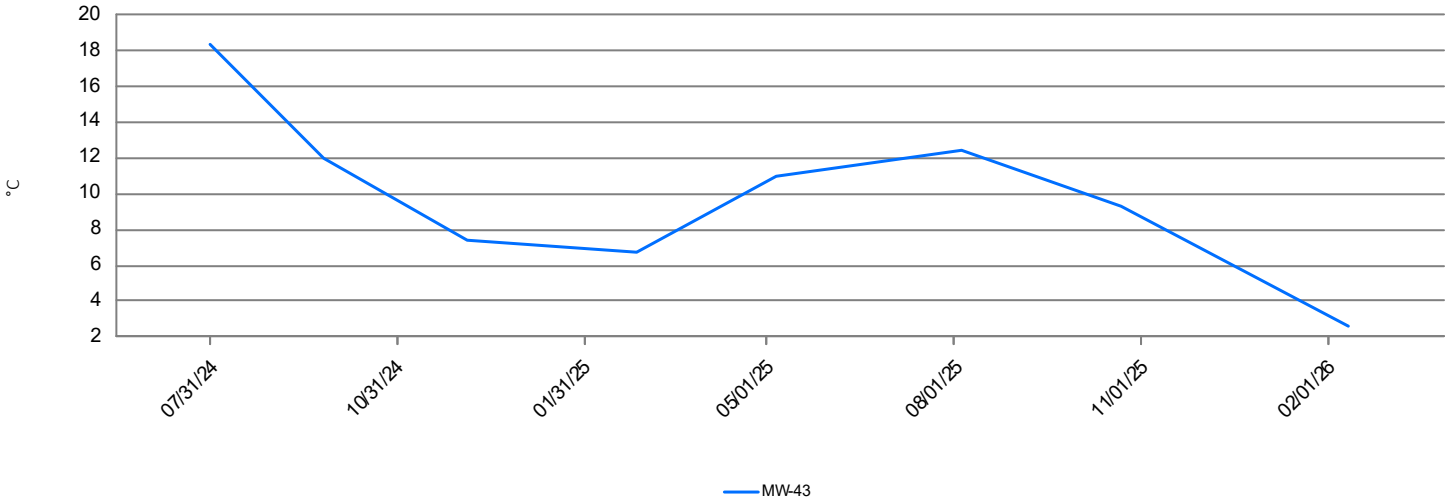
MonitorPro

No Group Selected, Temperature Field (°C)

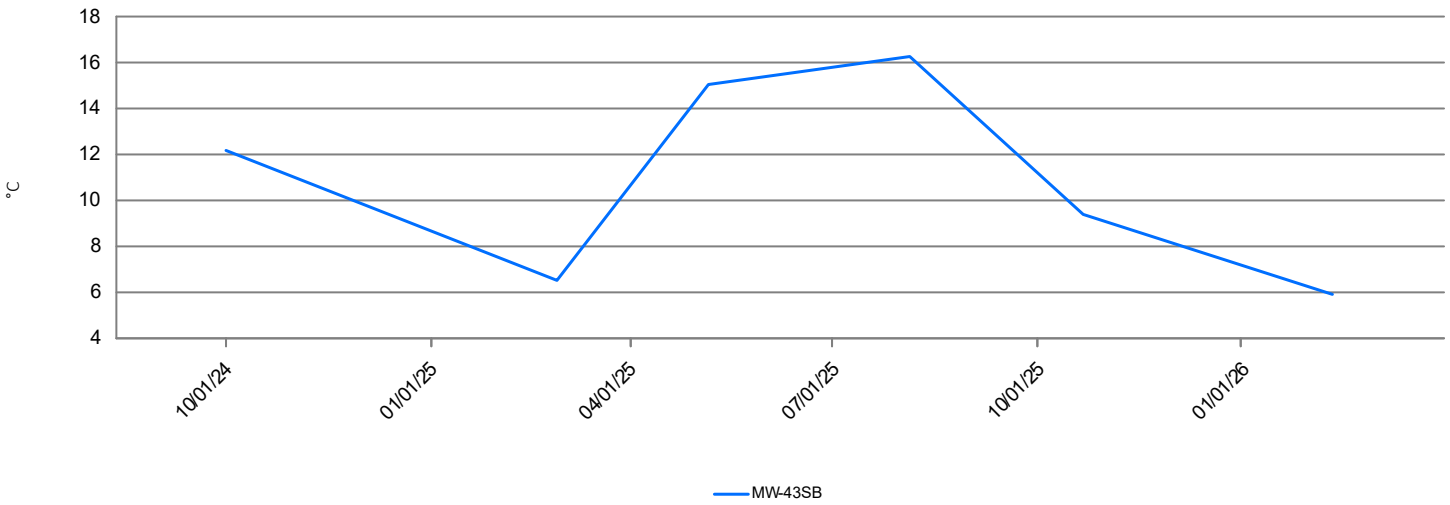
MW-42



MW-43



MW-43SB



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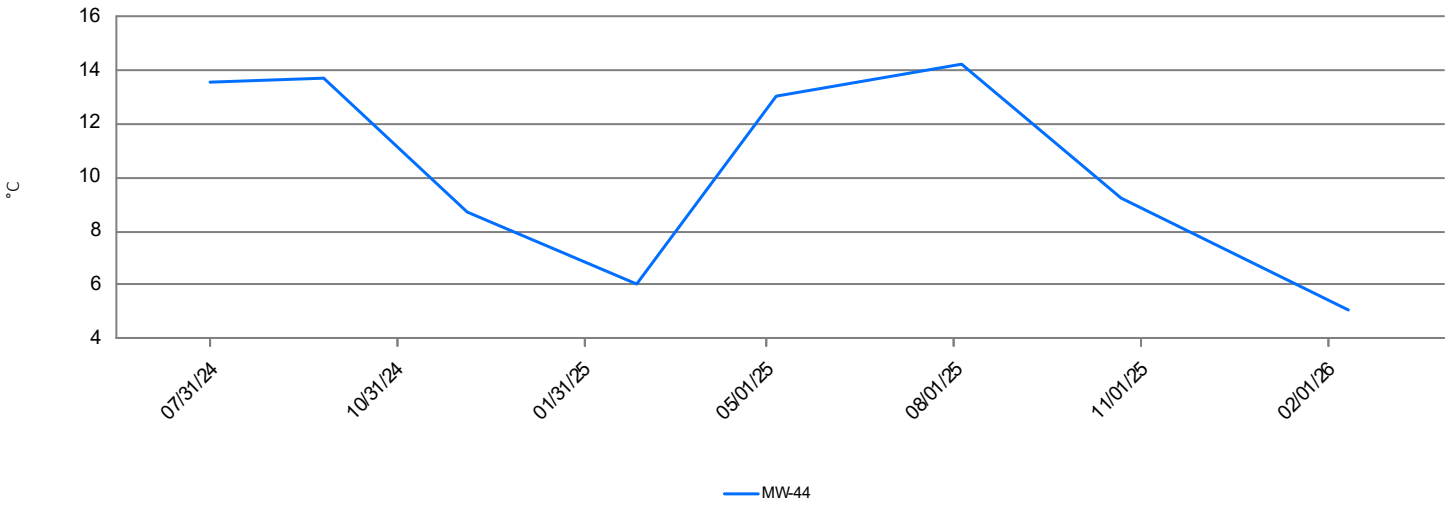
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

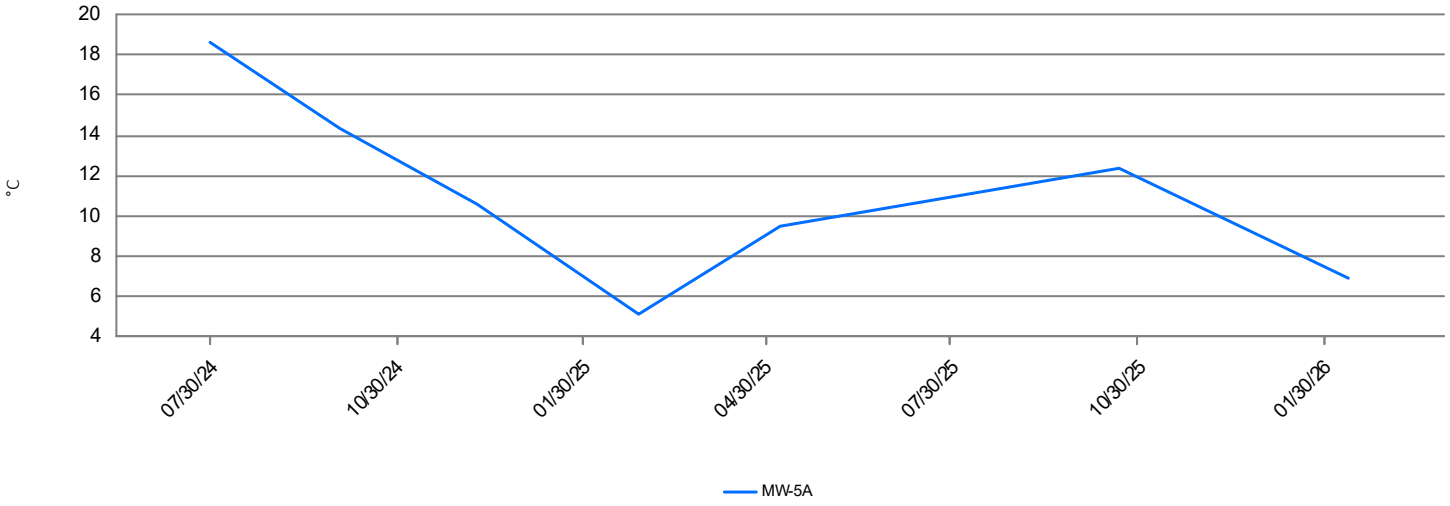
MonitorPro

No Group Selected, Temperature Field (°C)

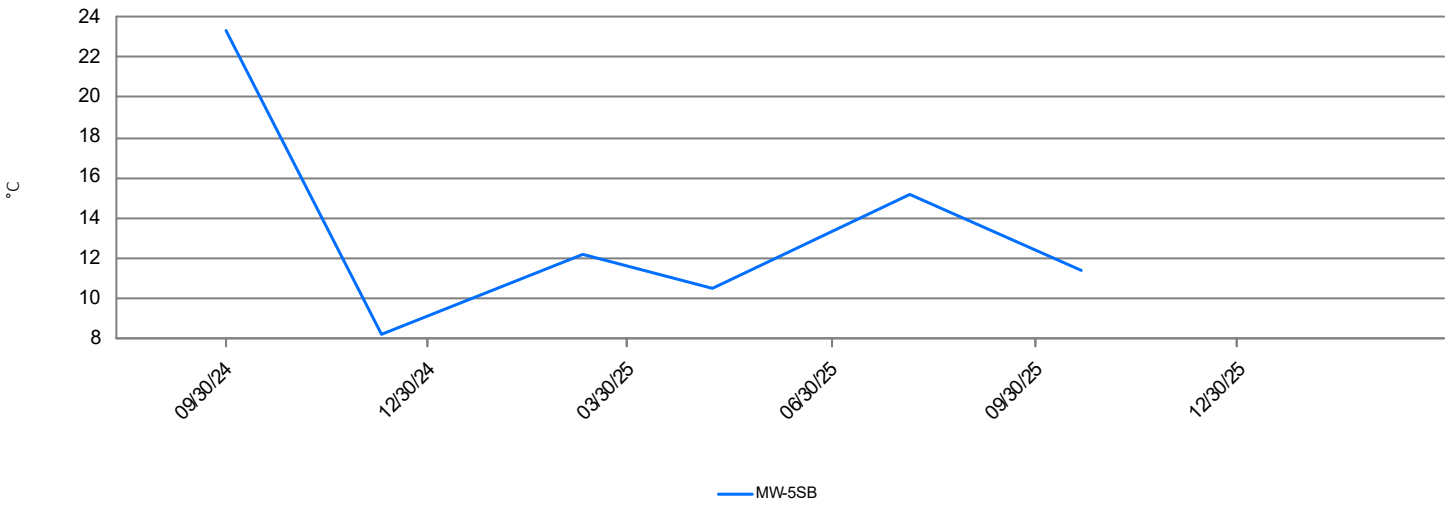
MW-44



MW-5A



MW-5SB

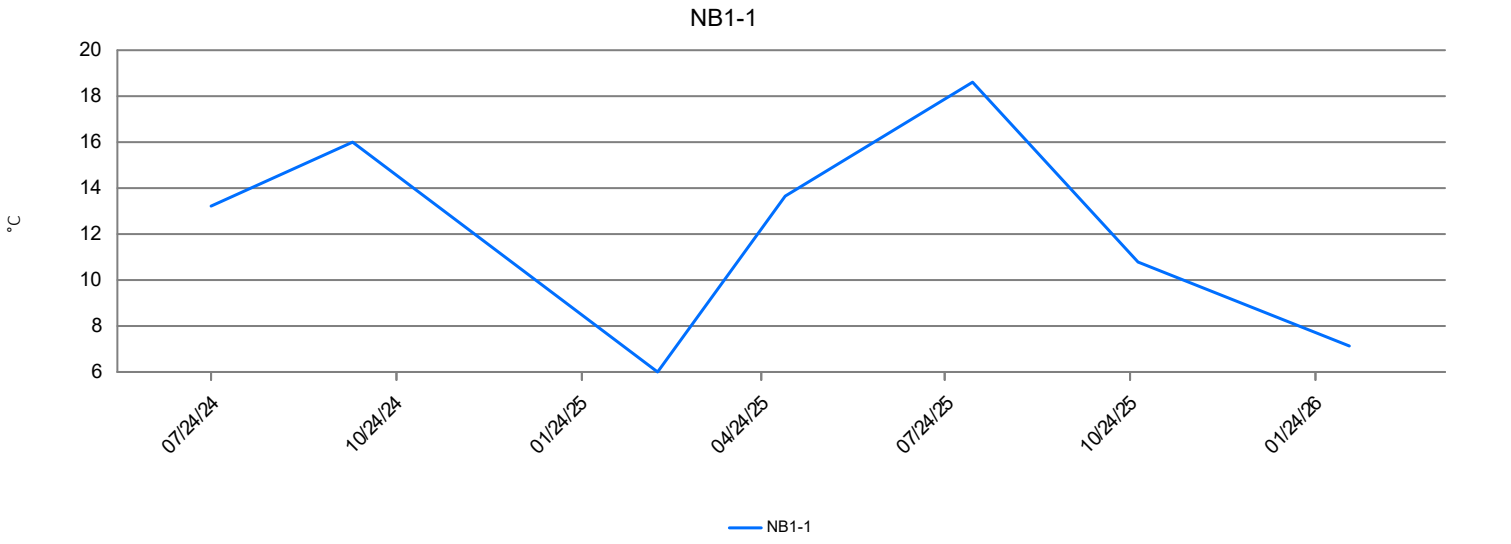


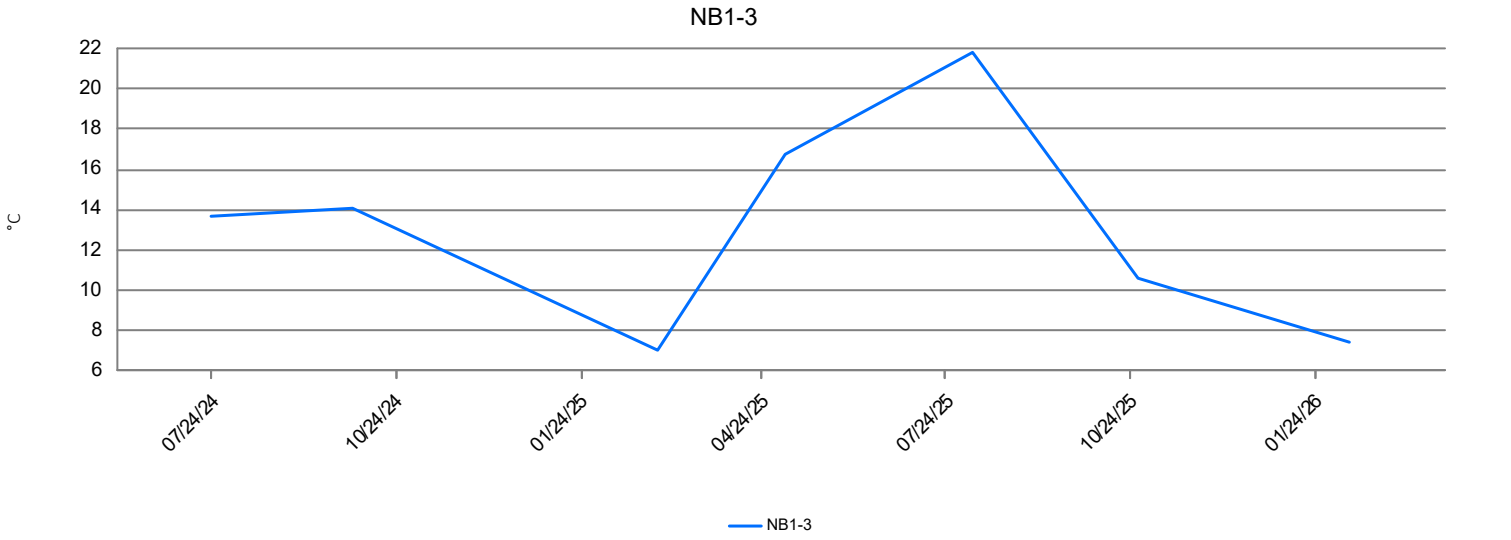
Variable Graphical Report

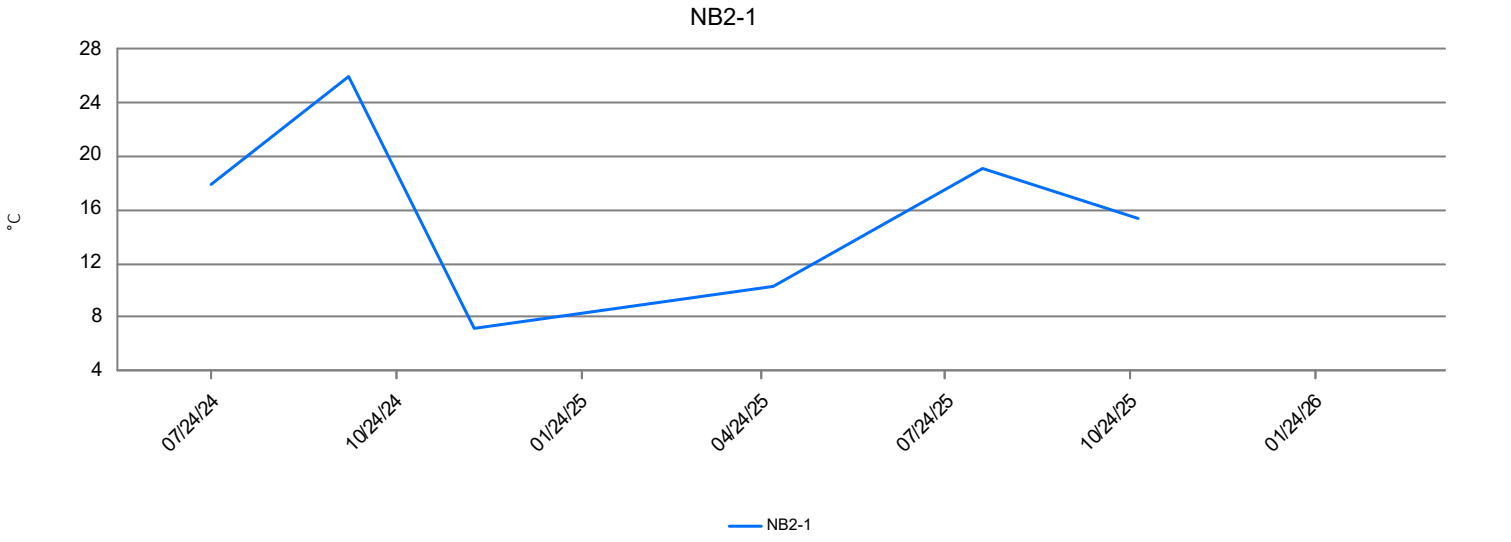
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Temperature Field (°C)





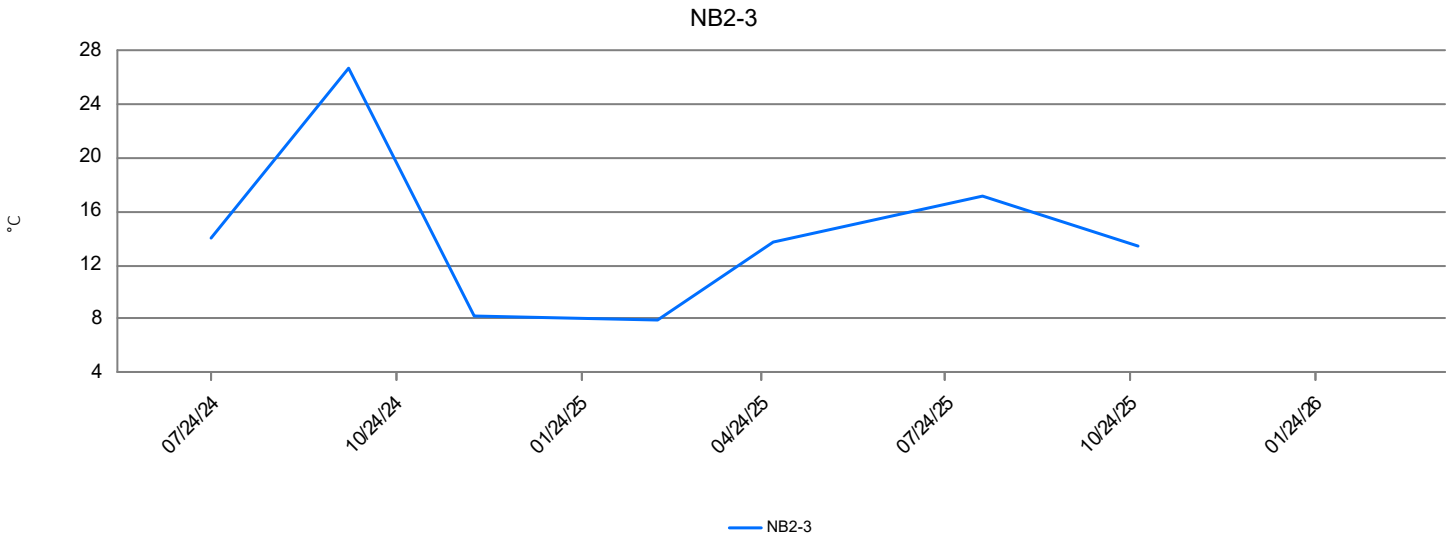


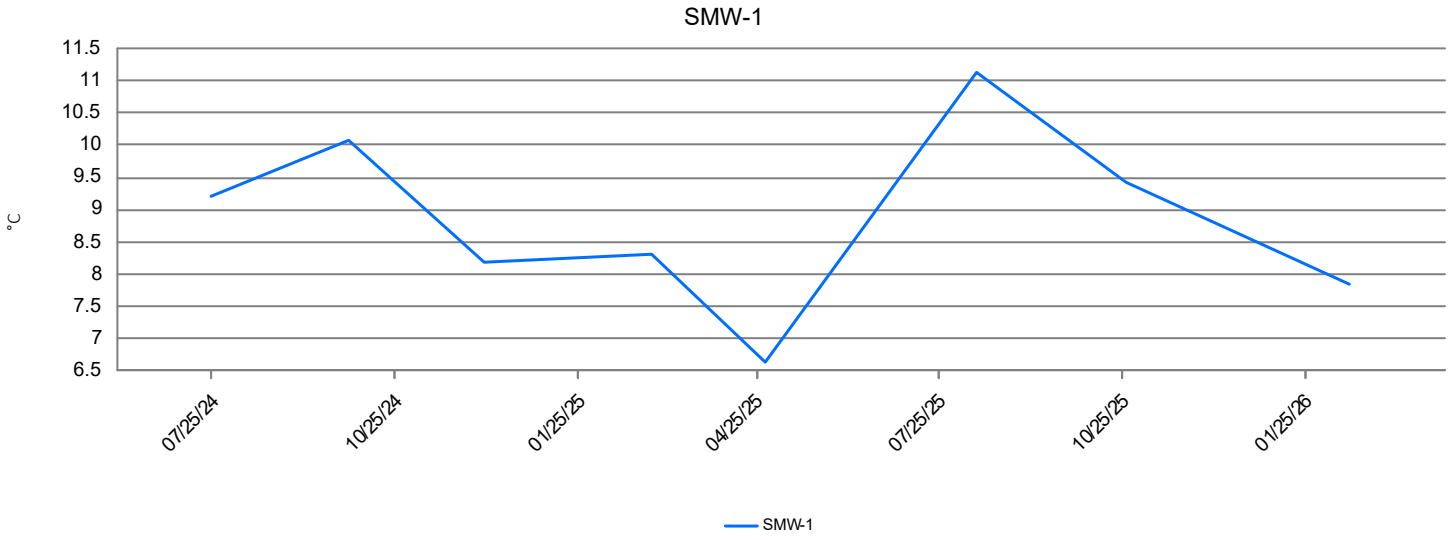
Variable Graphical Report

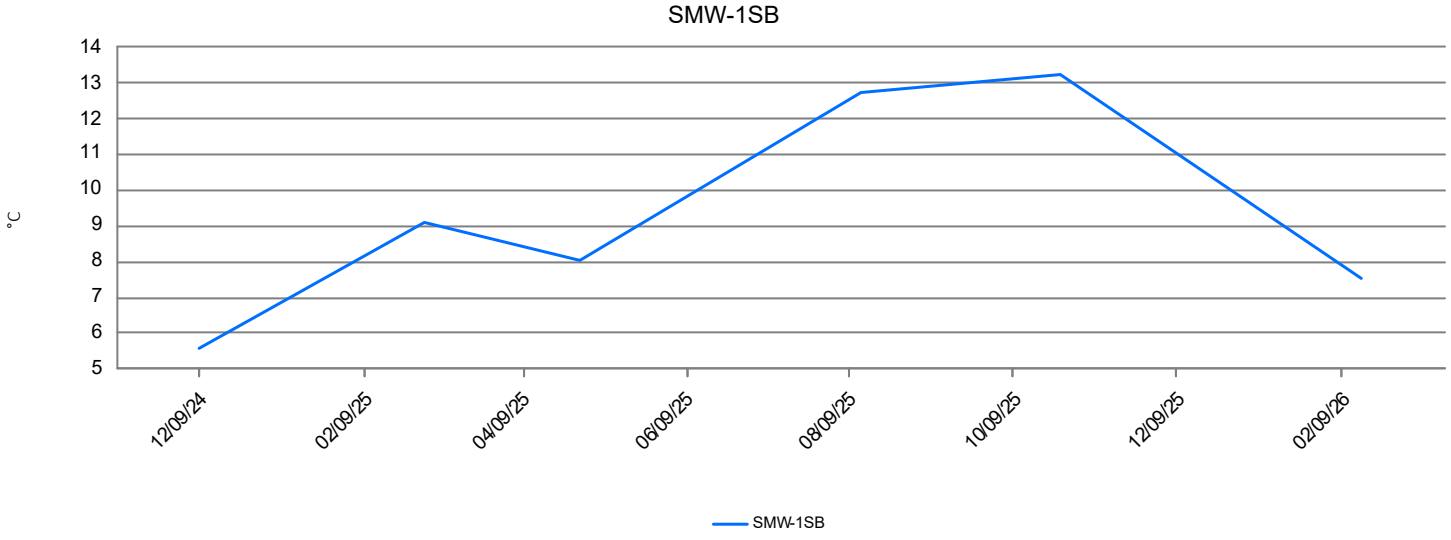
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Temperature Field (°C)







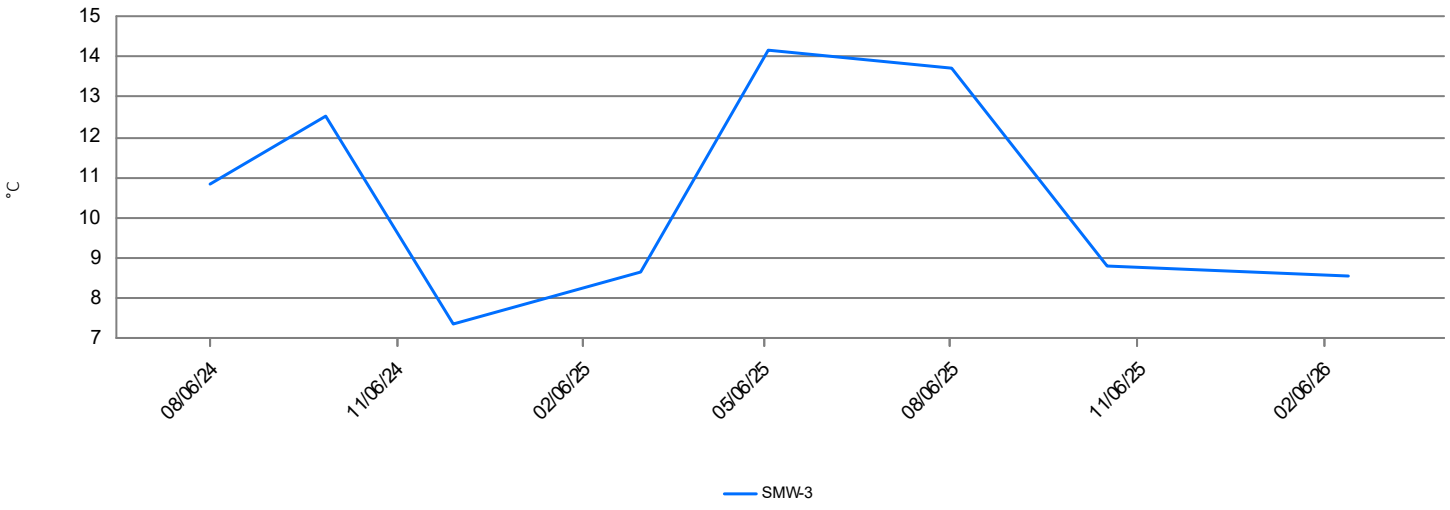
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

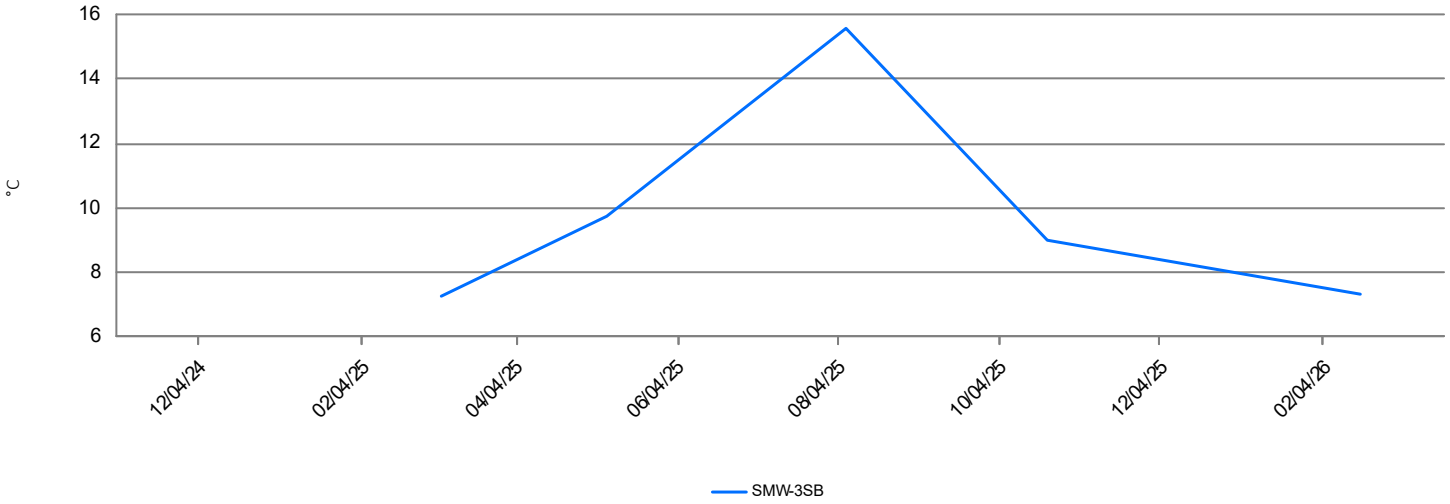
MonitorPro

No Group Selected, Temperature Field (°C)

SMW-3



SMW-3SB

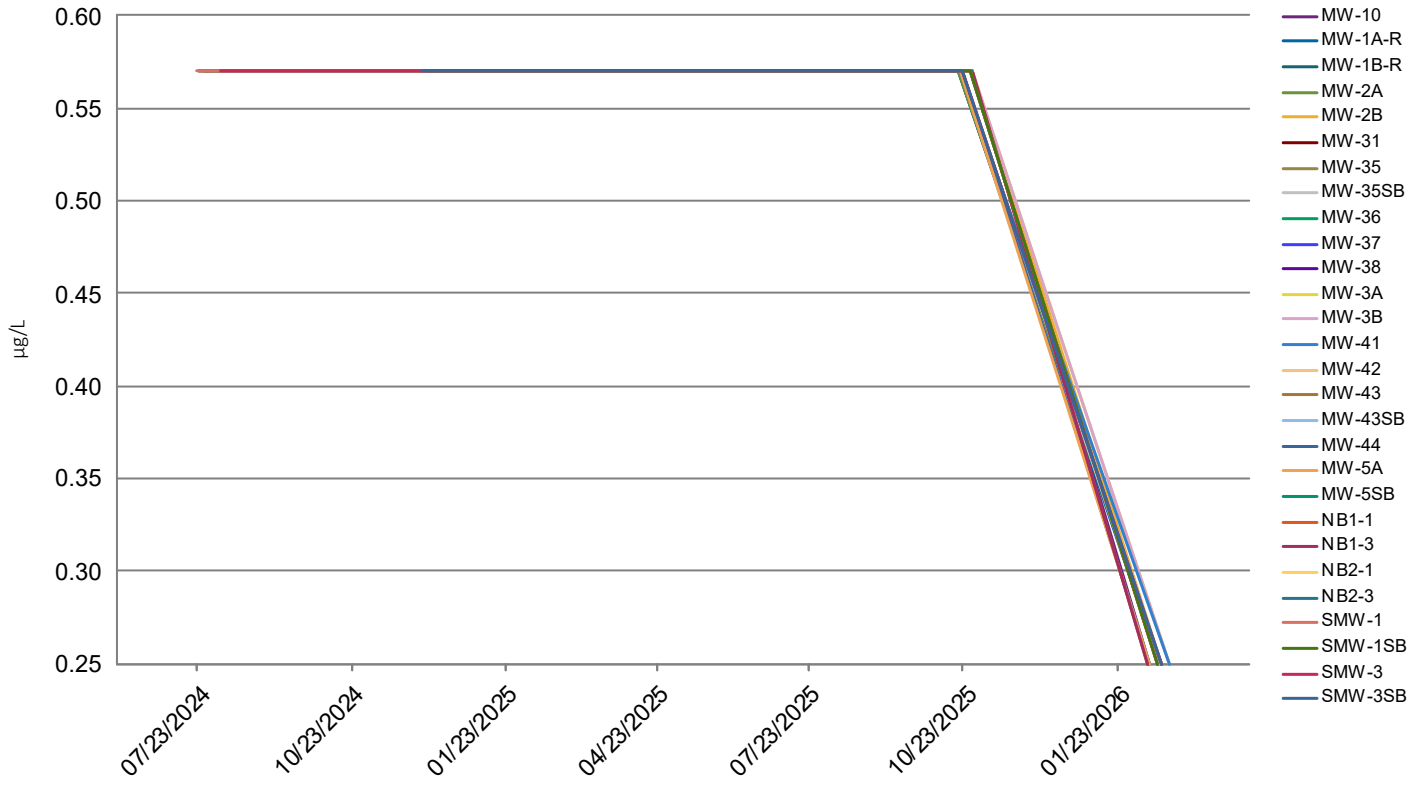


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Thallium, Dissolved (µg/L)

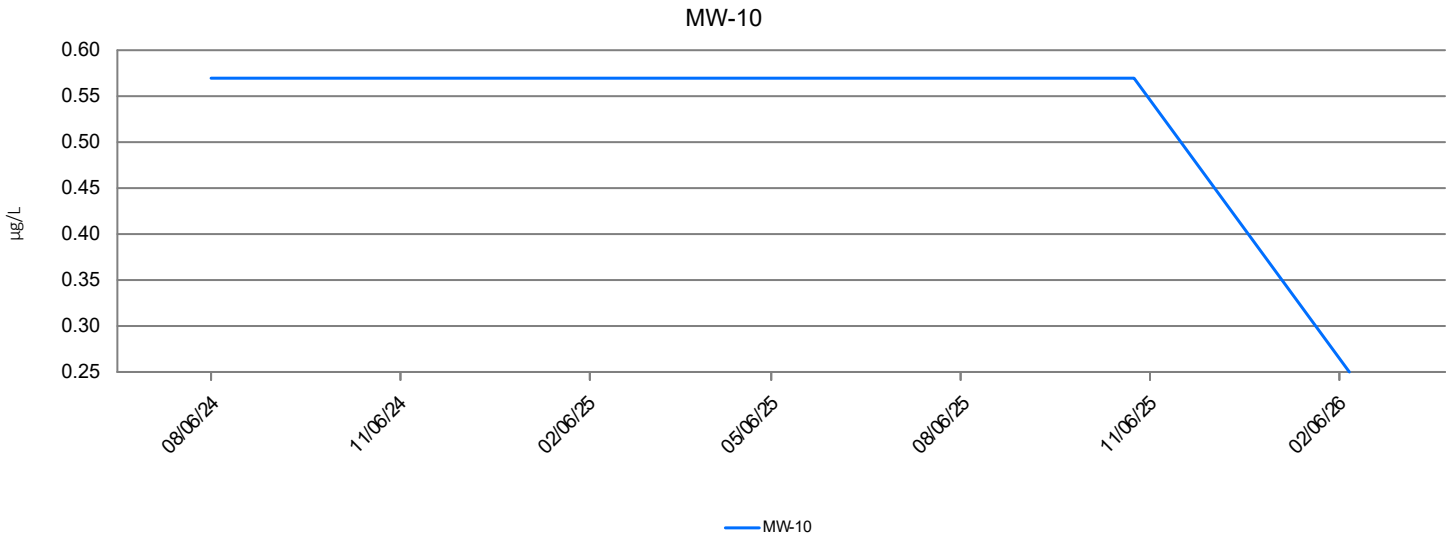


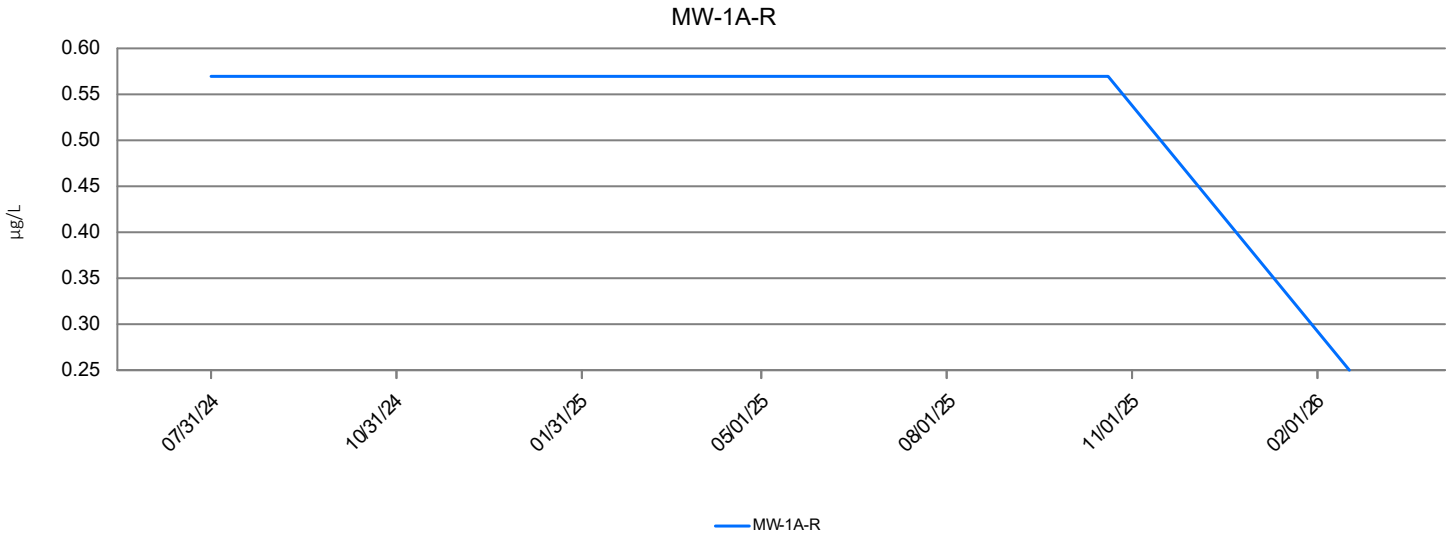
Variable Graphical Report

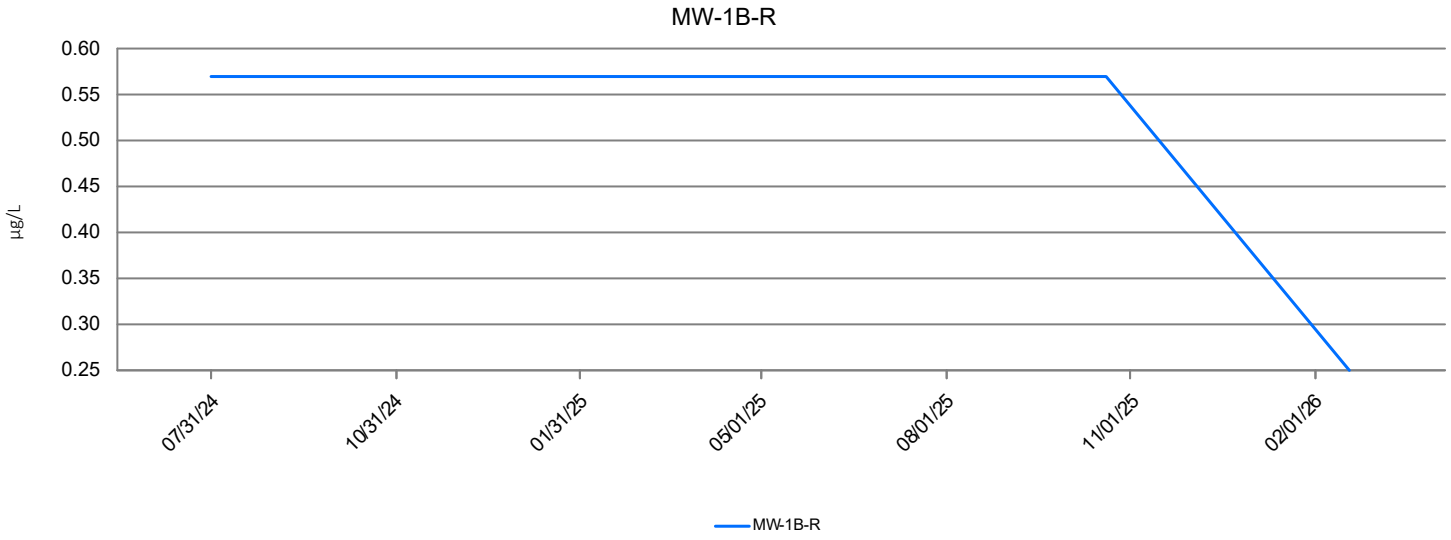
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Thallium, Dissolved (µg/L)







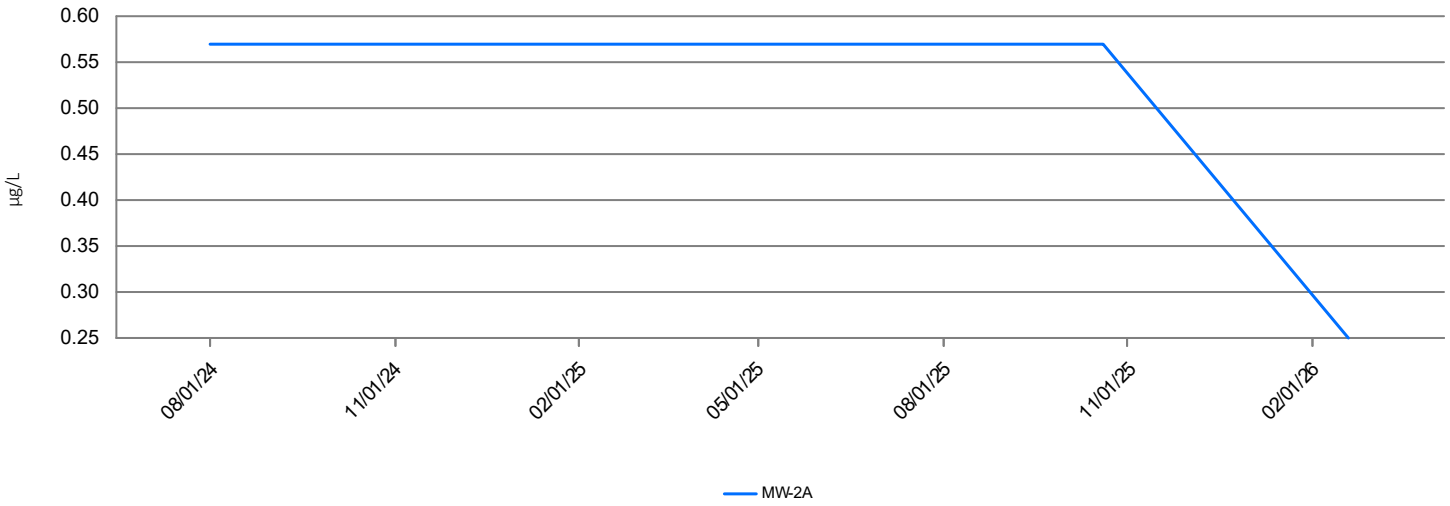
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

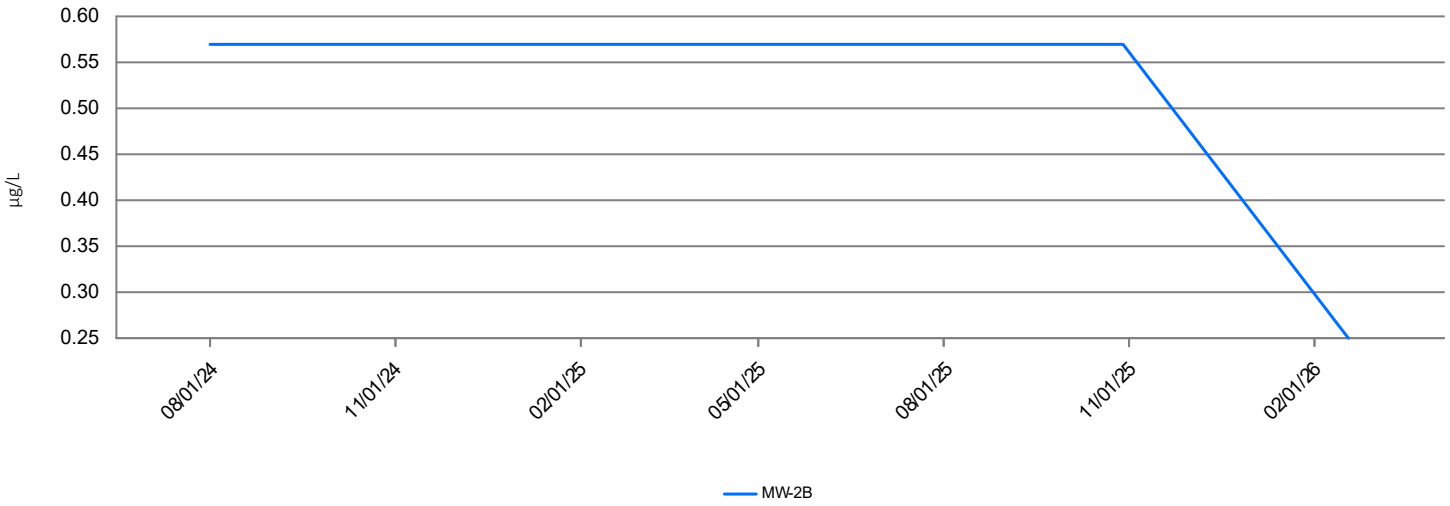
MonitorPro

No Group Selected, Thallium, Dissolved (µg/L)

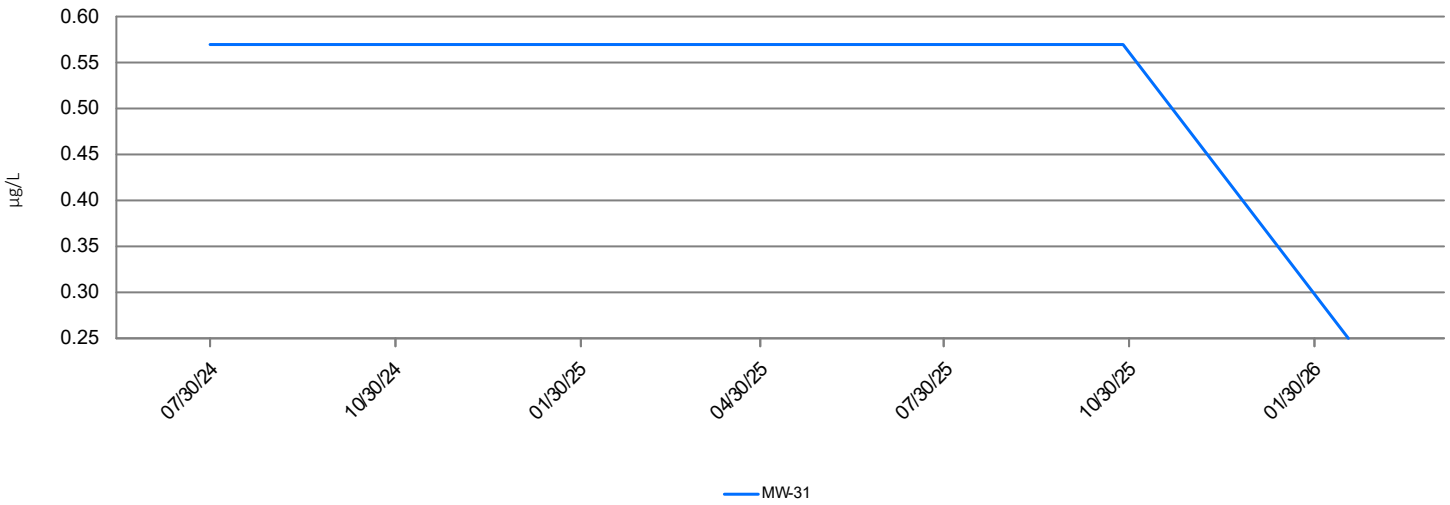
MW-2A



MW-2B



MW-31

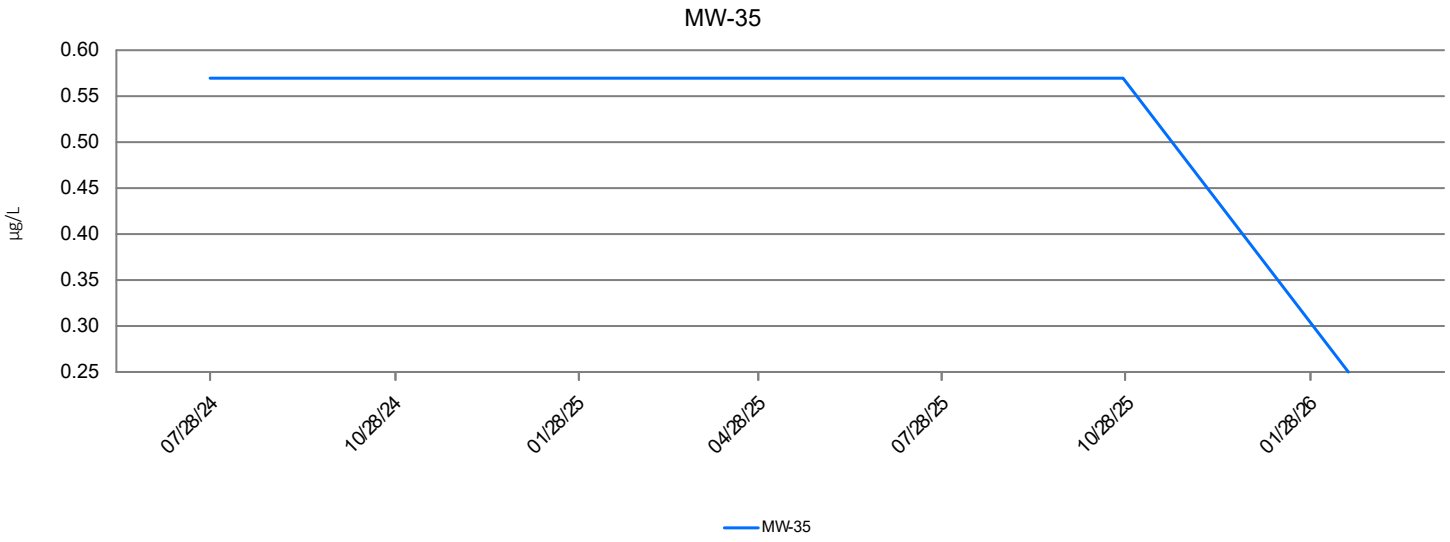


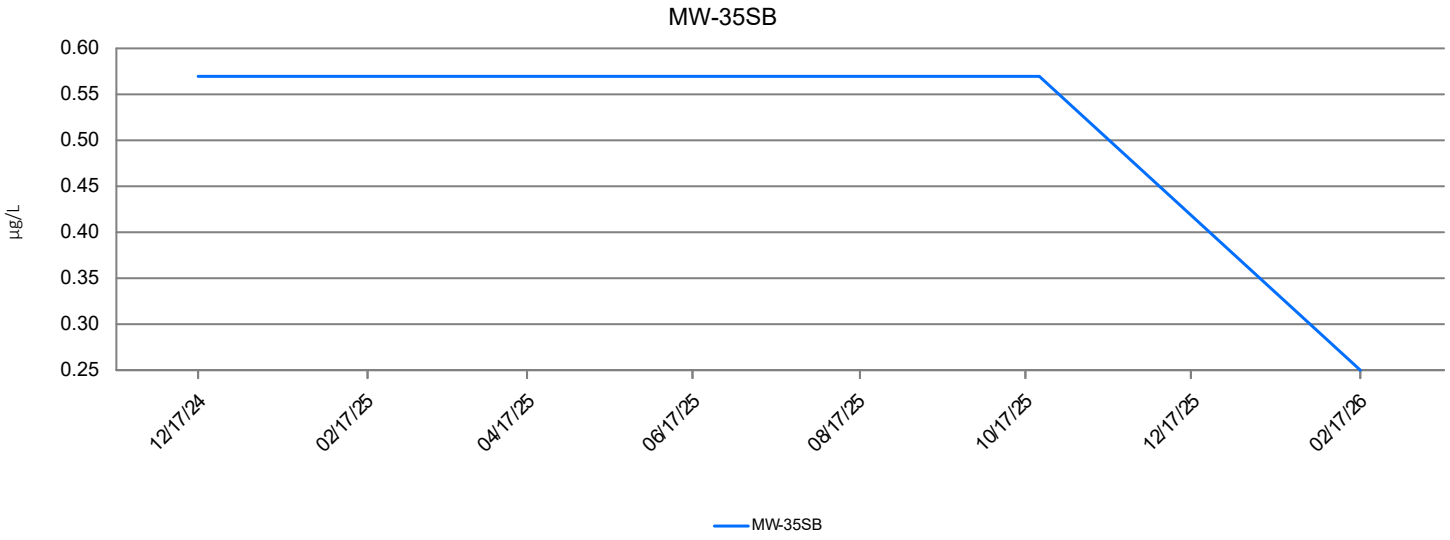
Variable Graphical Report

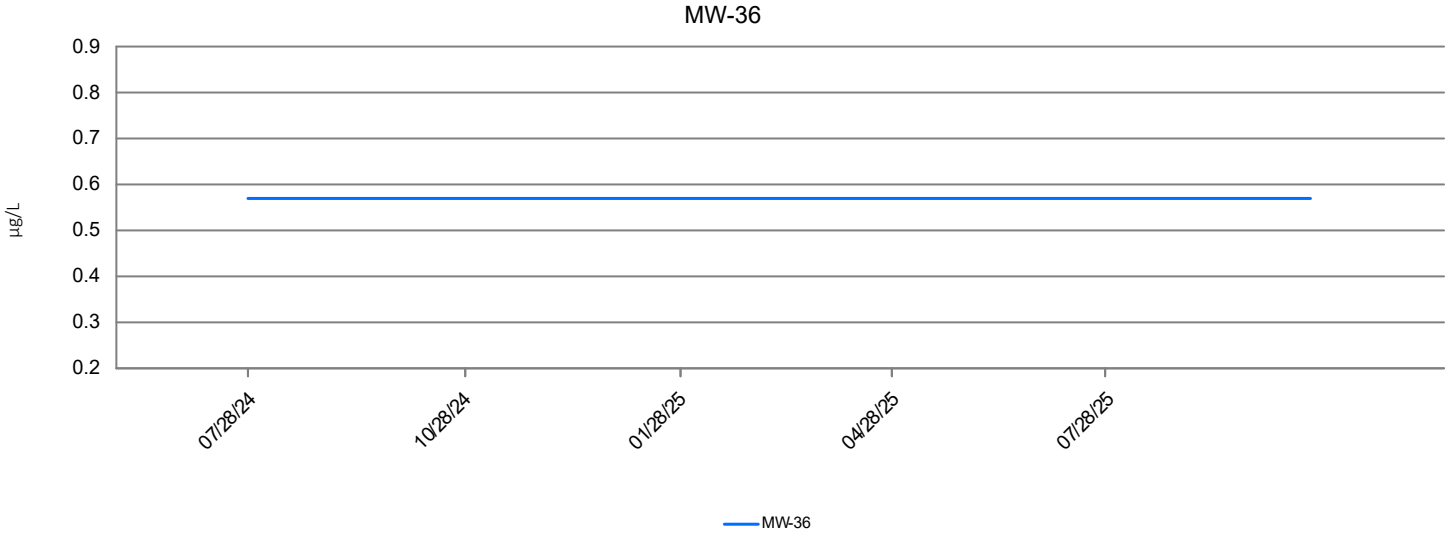
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Thallium, Dissolved (µg/L)





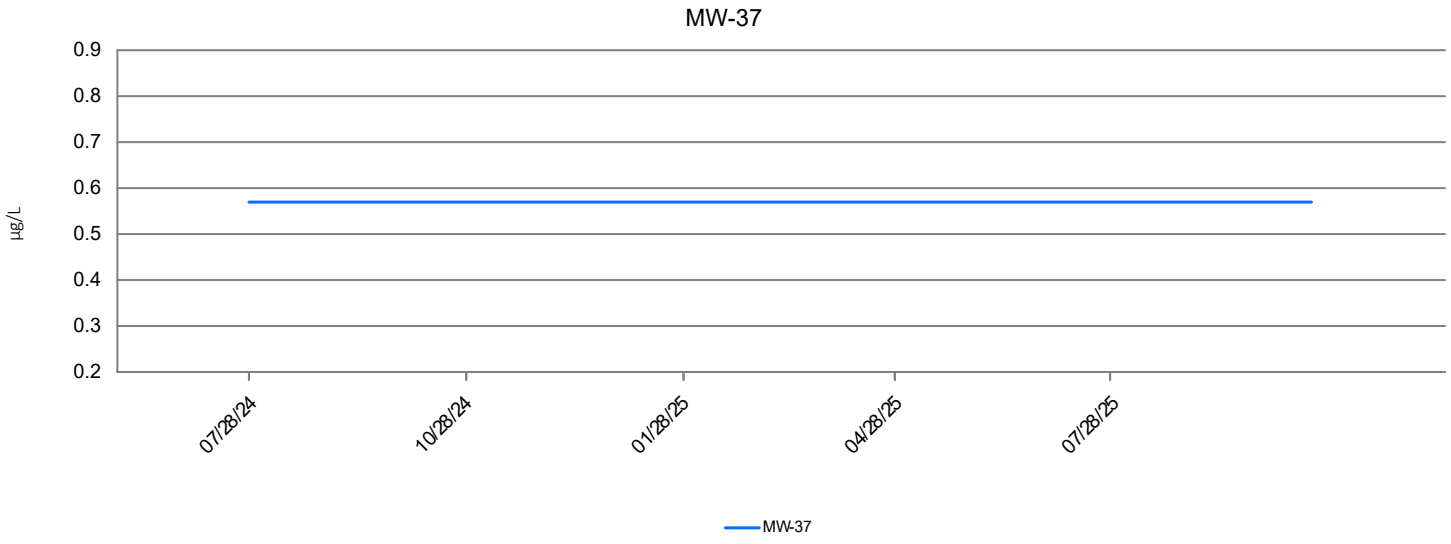


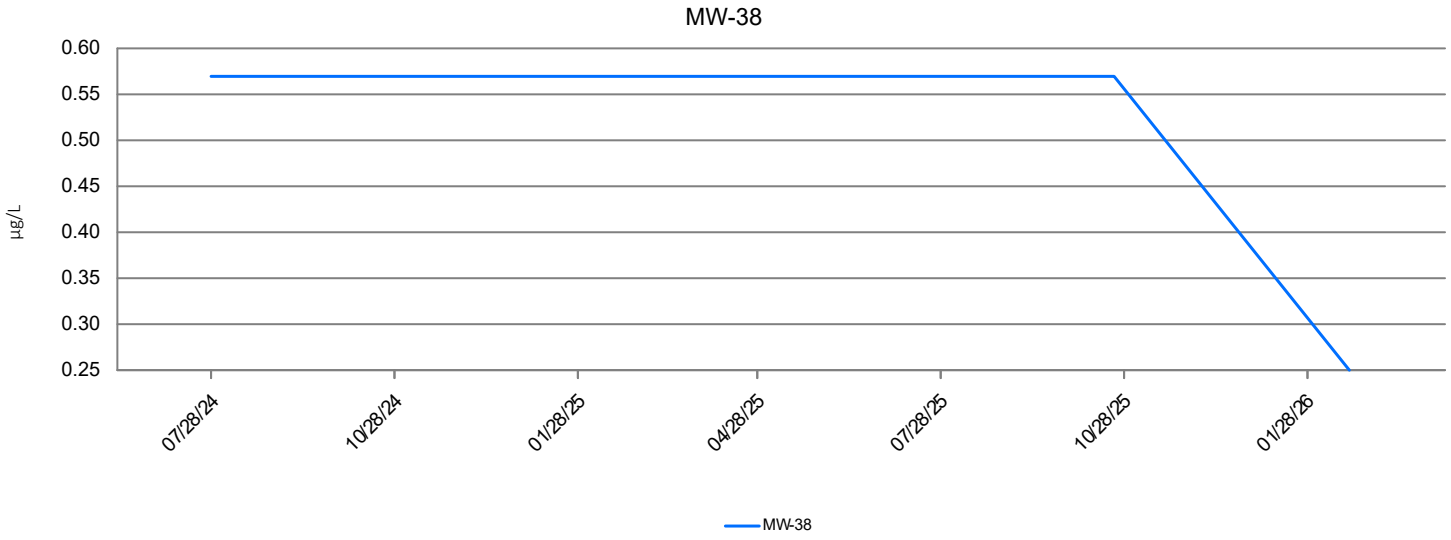
Variable Graphical Report

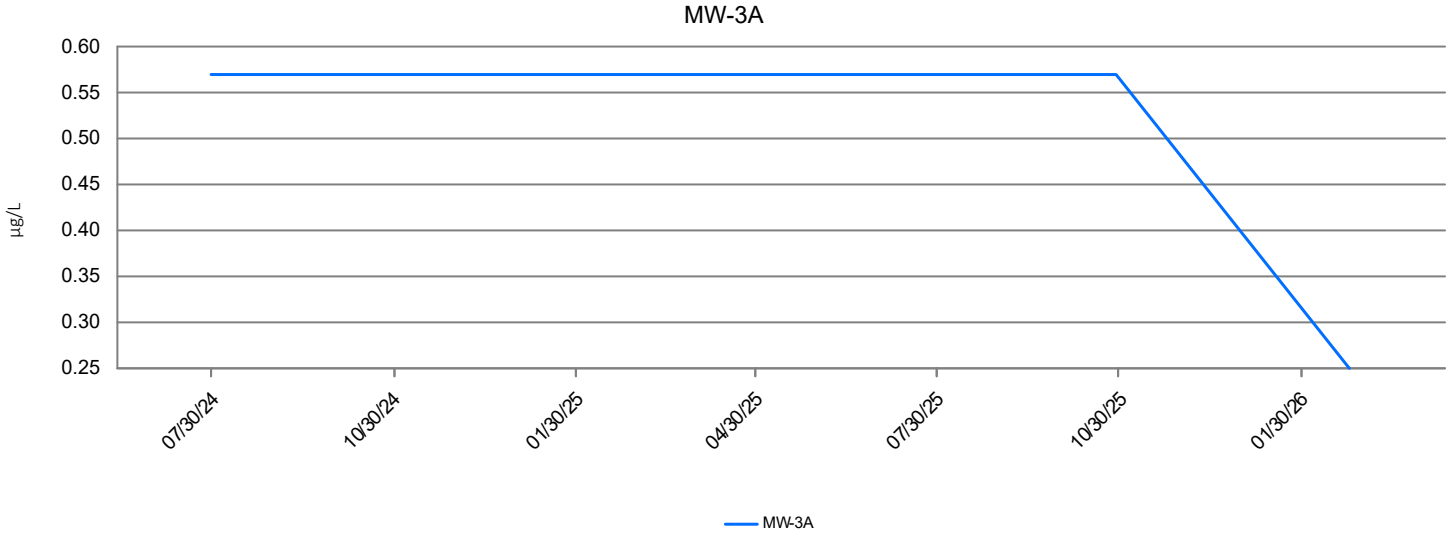
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Thallium, Dissolved (µg/L)







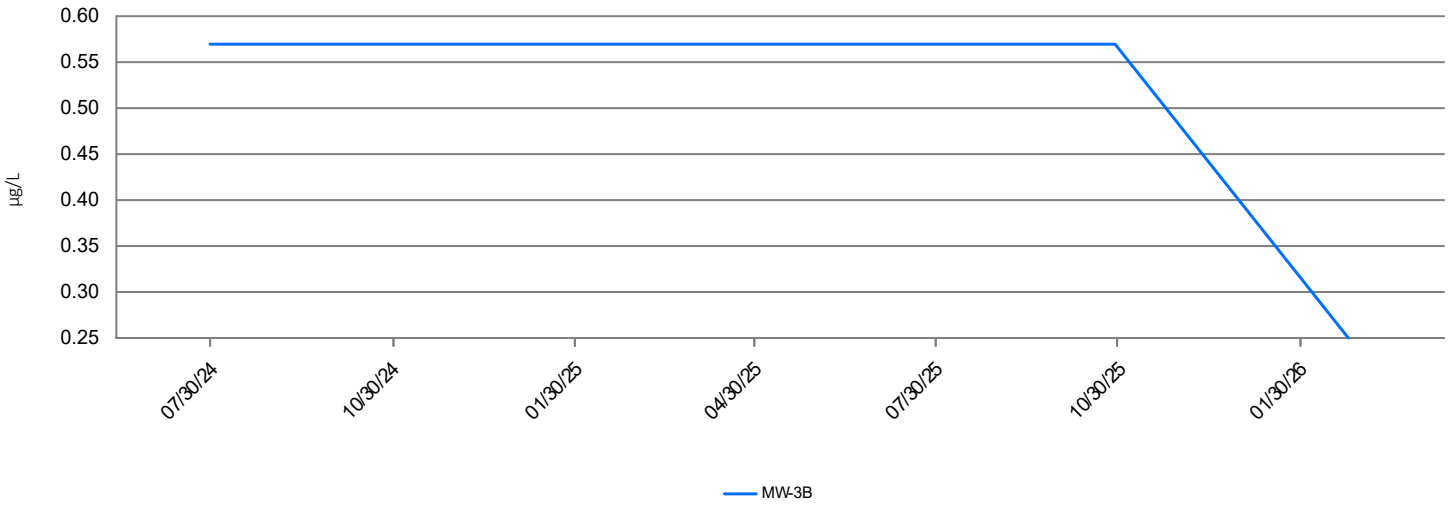
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

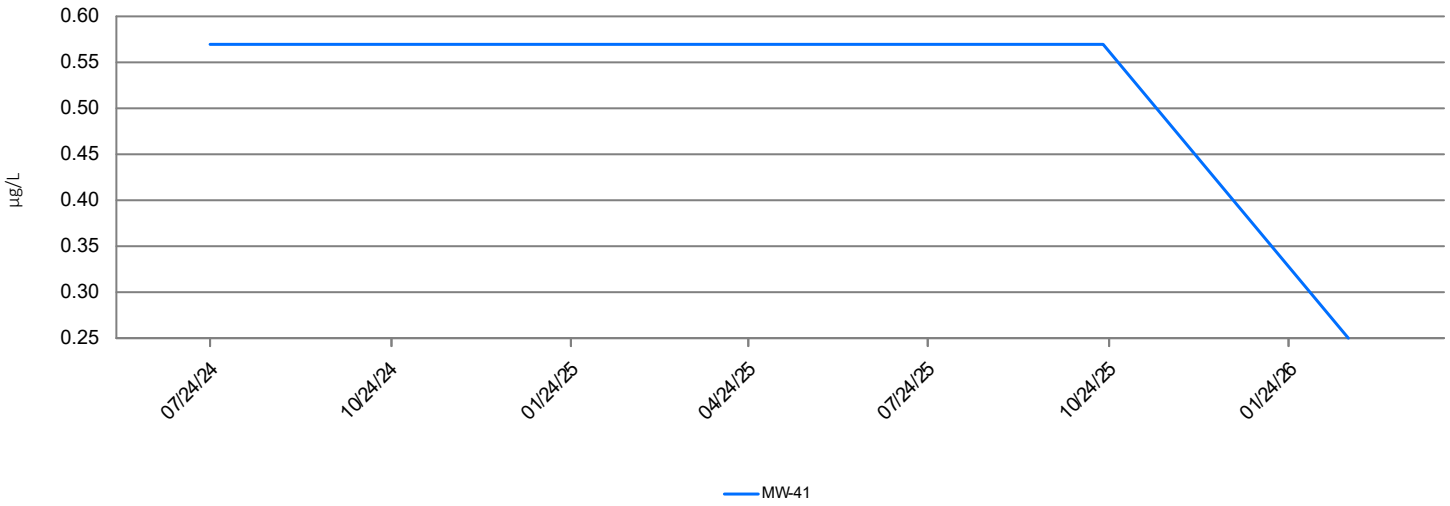
MonitorPro

No Group Selected, Thallium, Dissolved (µg/L)

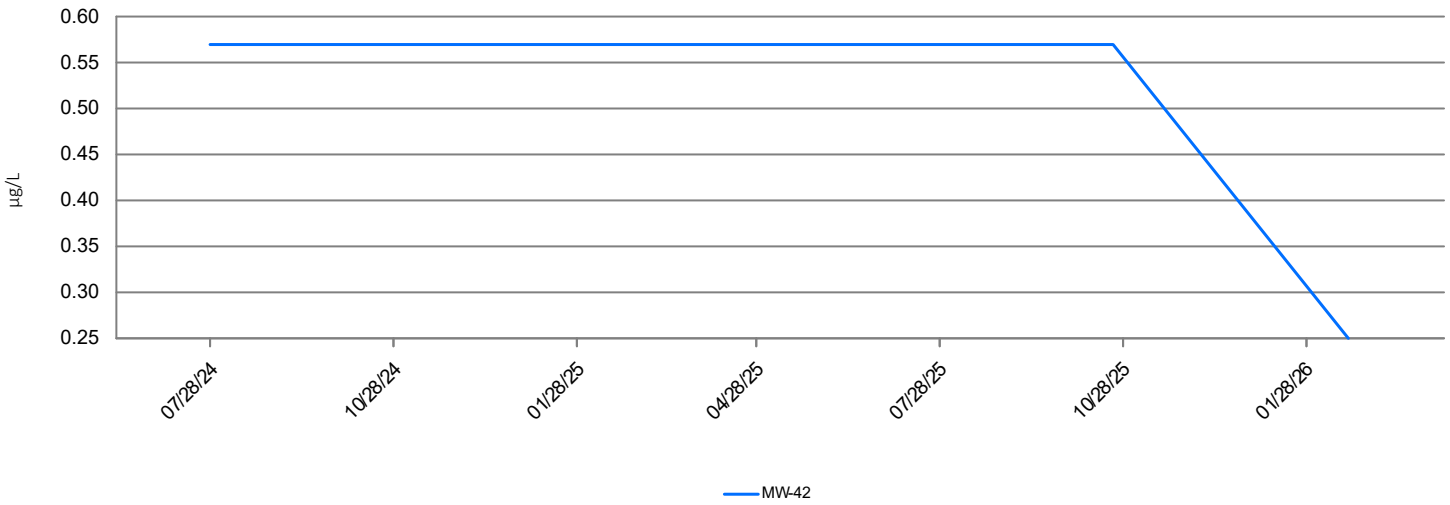
MW-3B



MW-41



MW-42

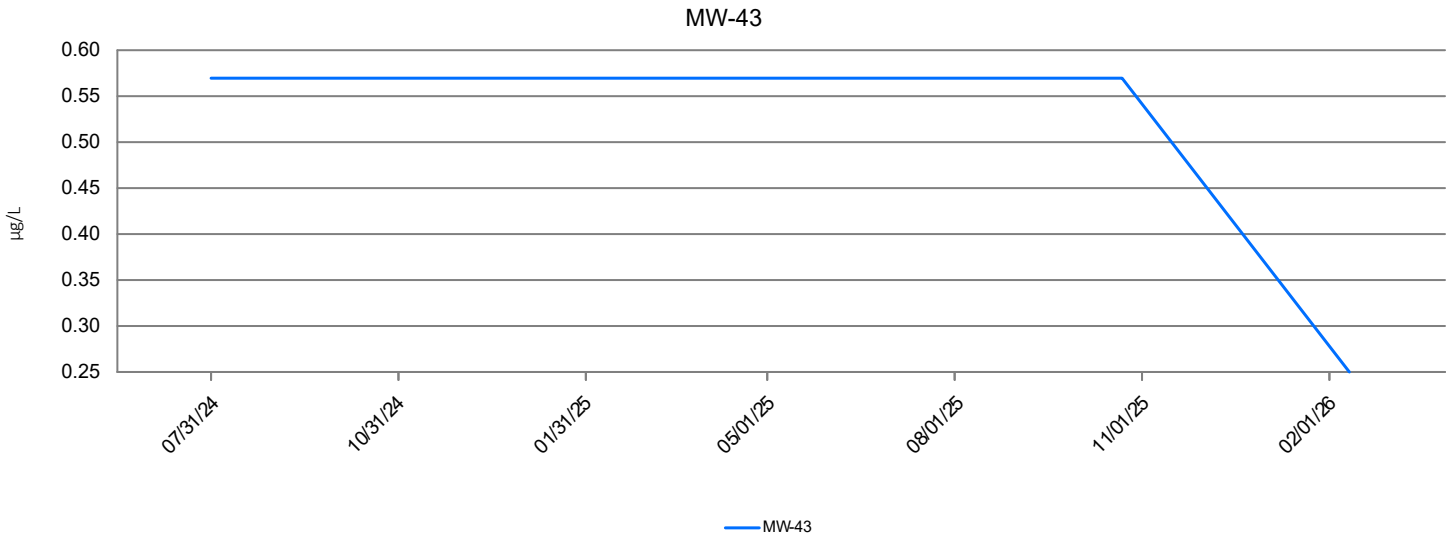


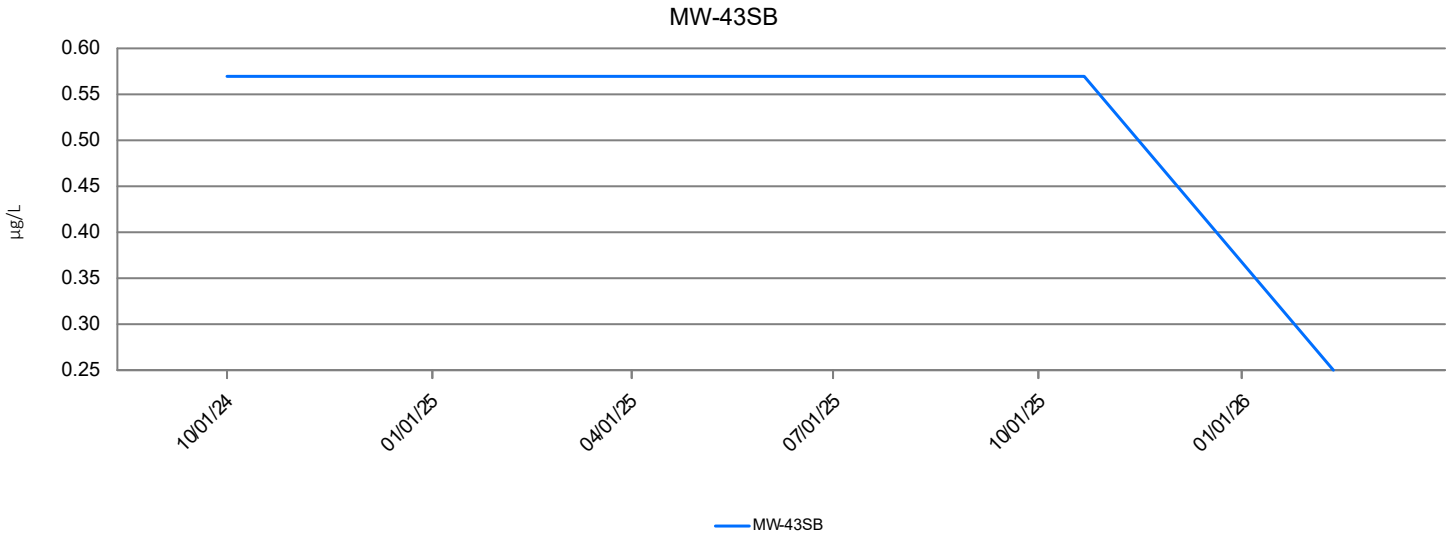
Variable Graphical Report

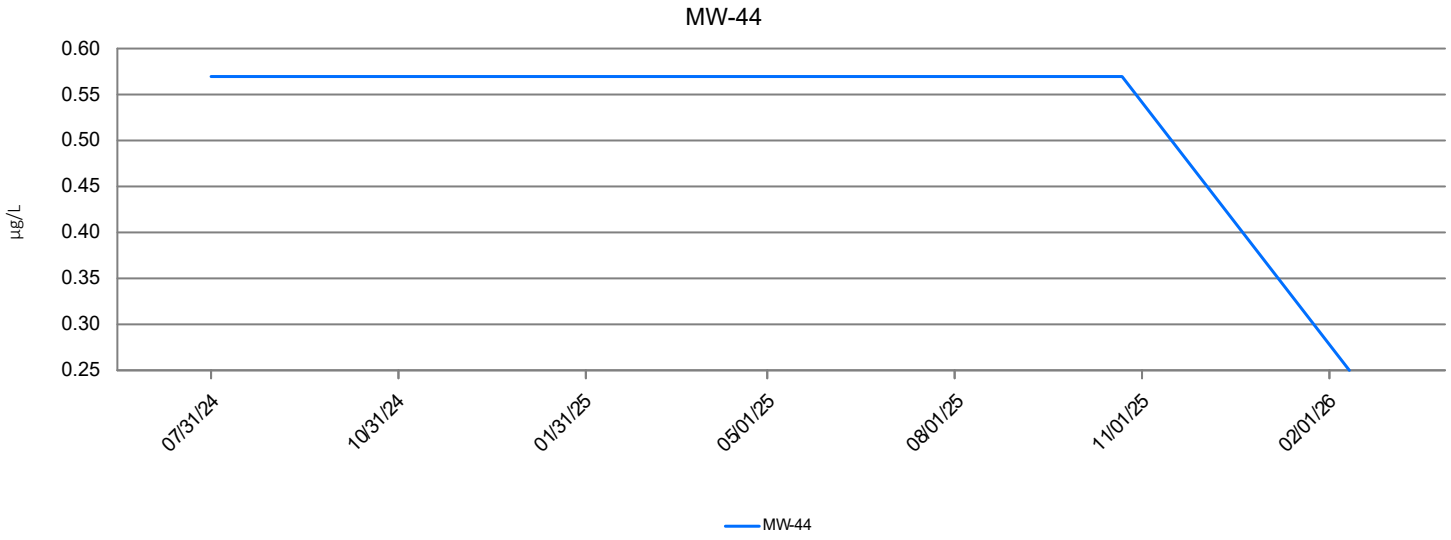
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Thallium, Dissolved (µg/L)







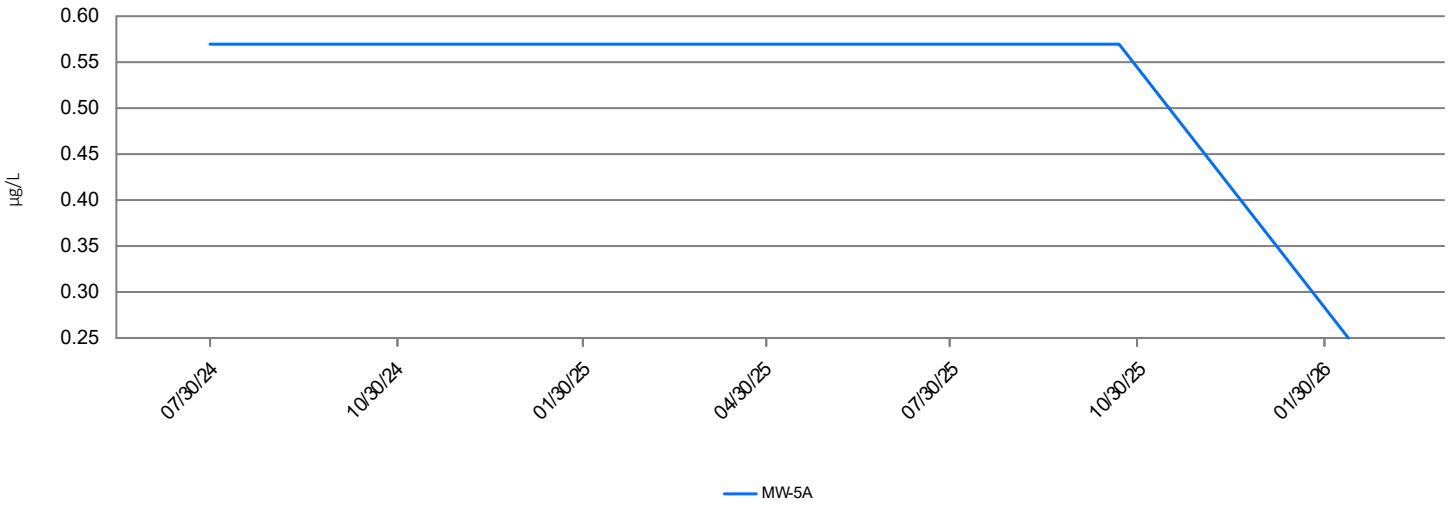
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

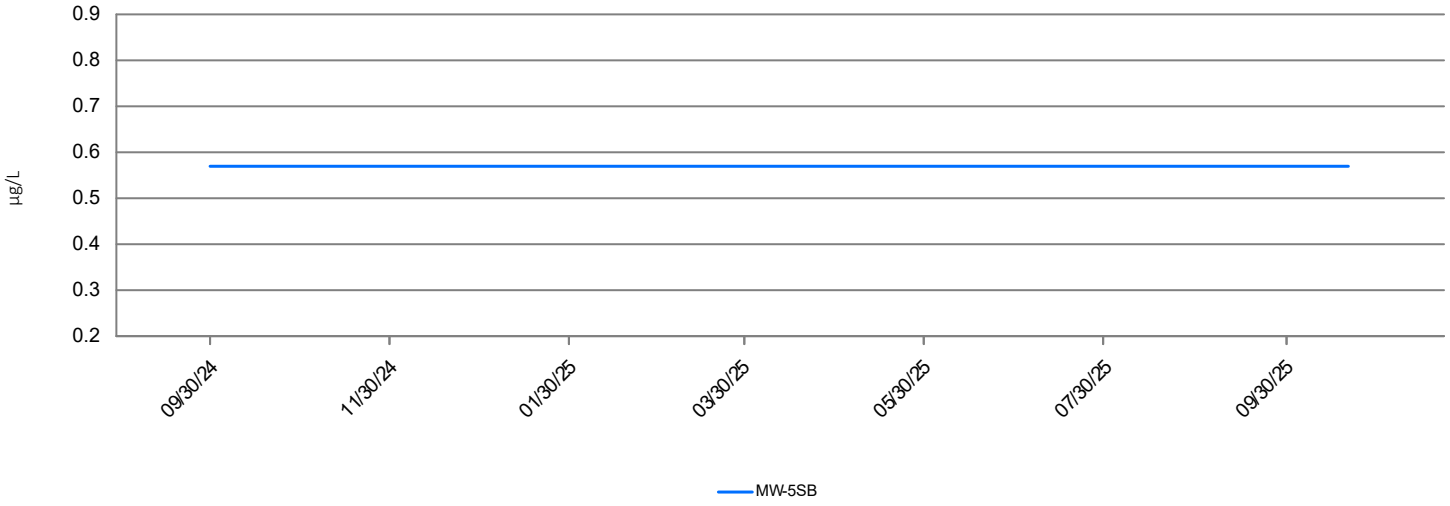
MonitorPro

No Group Selected, Thallium, Dissolved (µg/L)

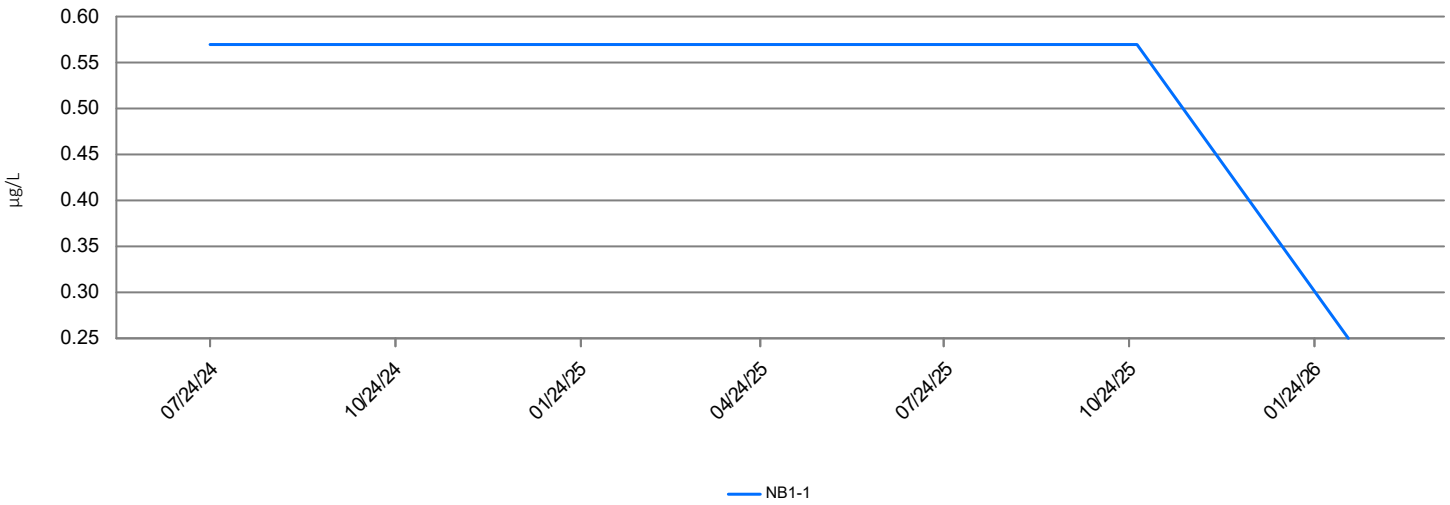
MW-5A



MW-5SB



NB1-1

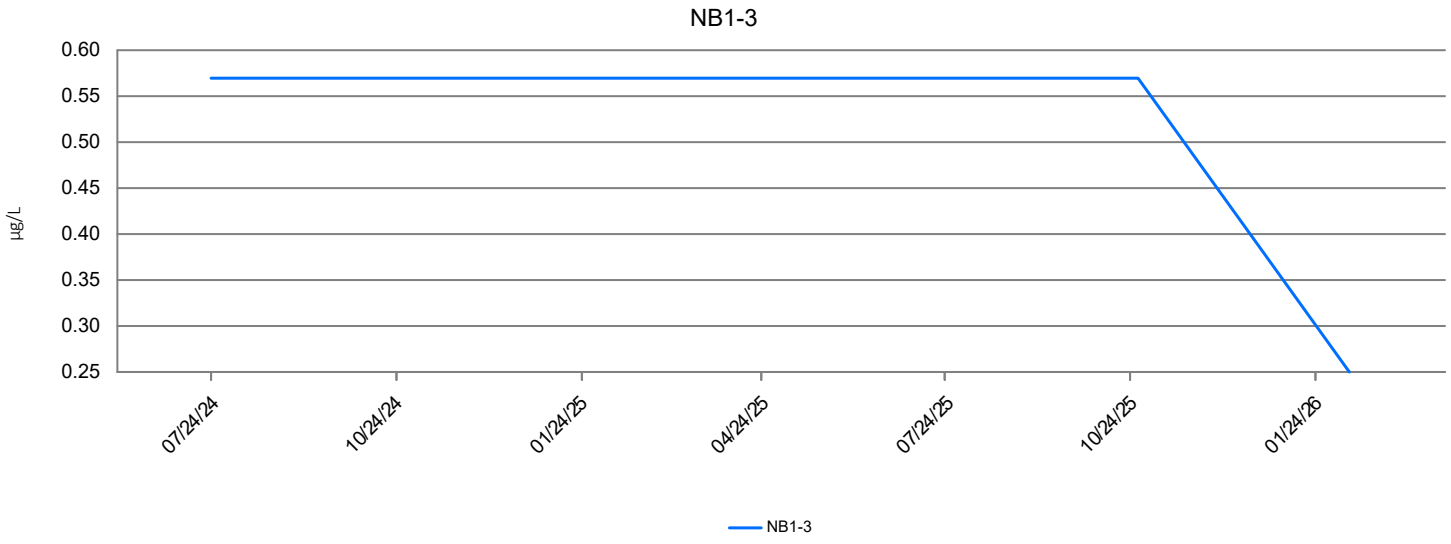


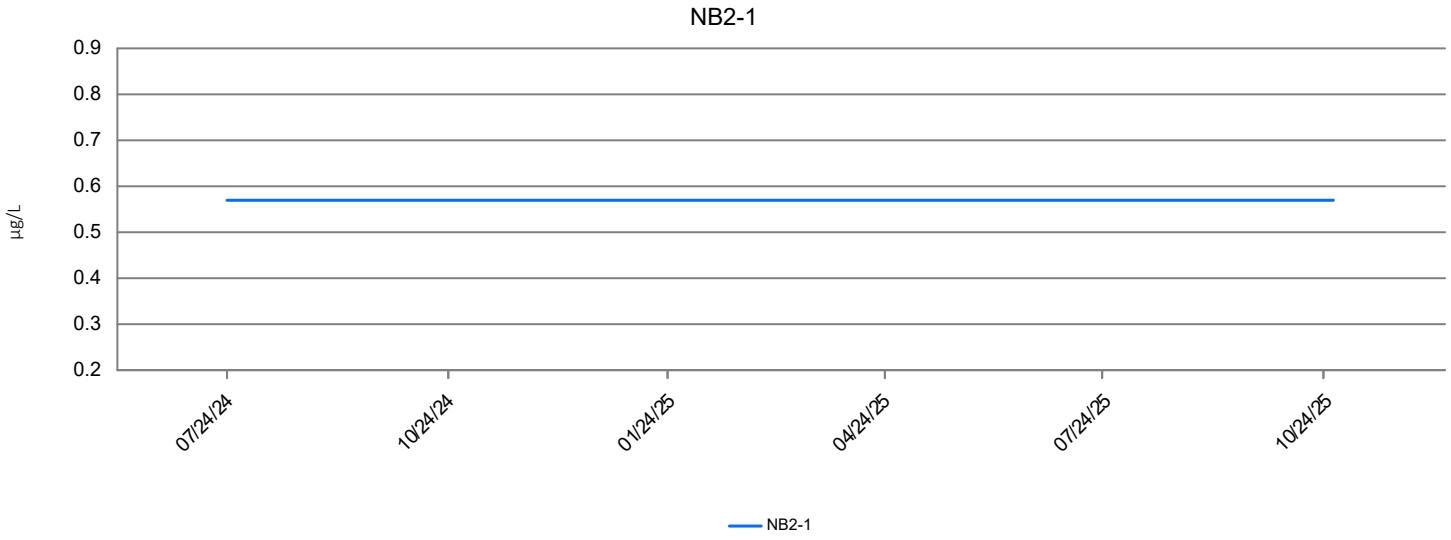
Variable Graphical Report

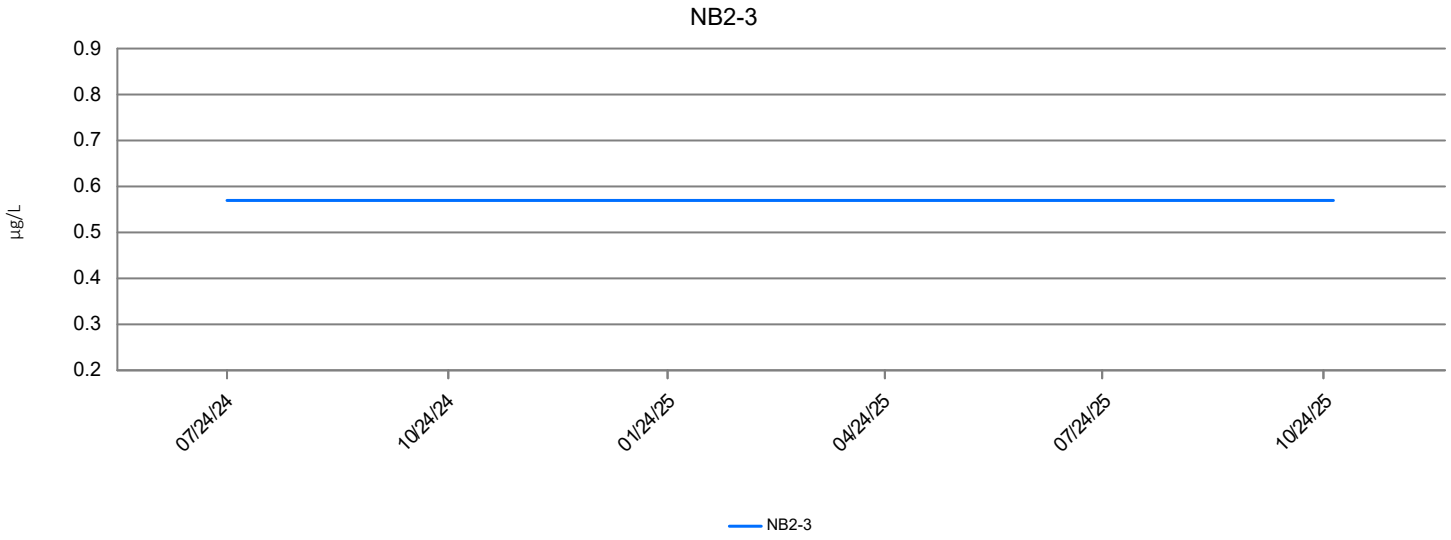
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Thallium, Dissolved (µg/L)







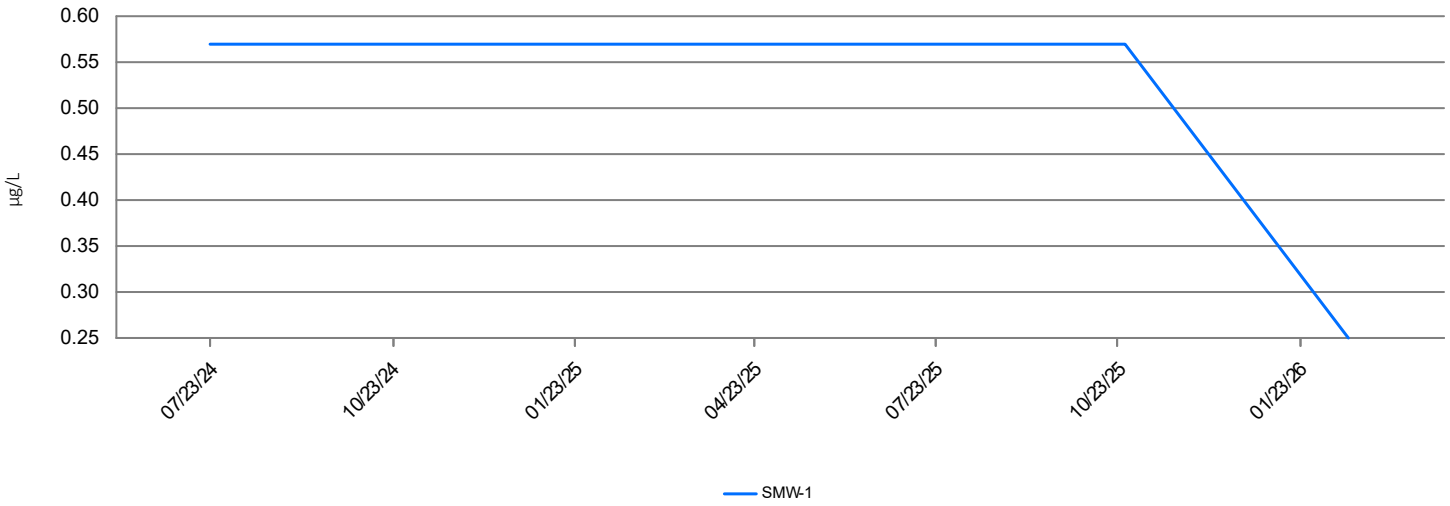
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

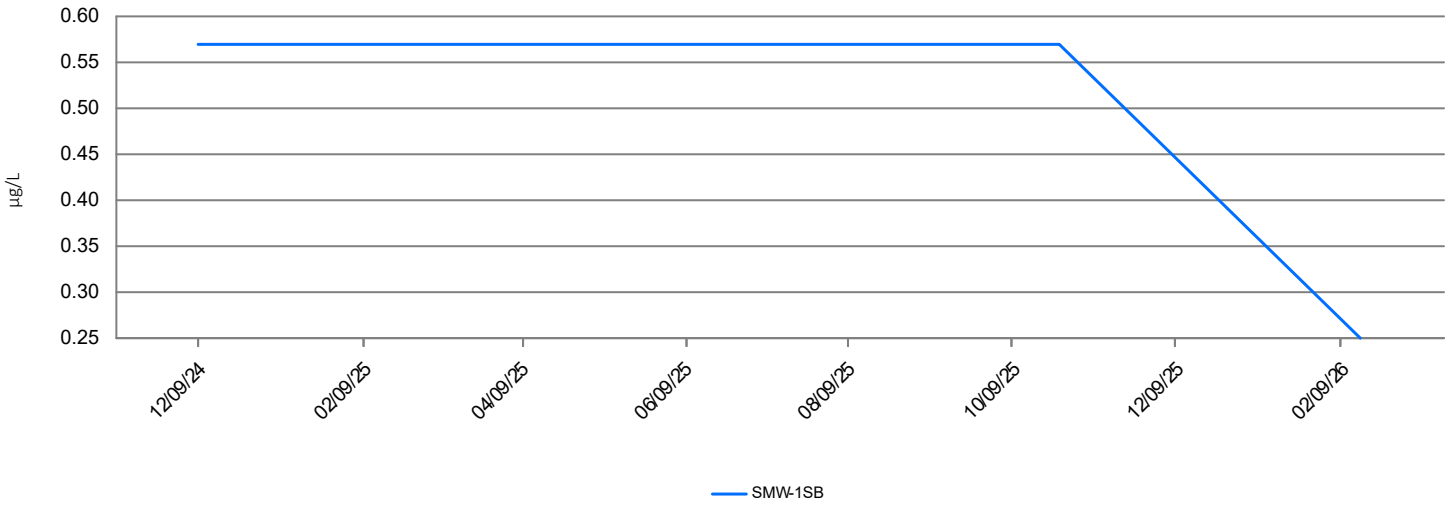
MonitorPro

No Group Selected, Thallium, Dissolved (µg/L)

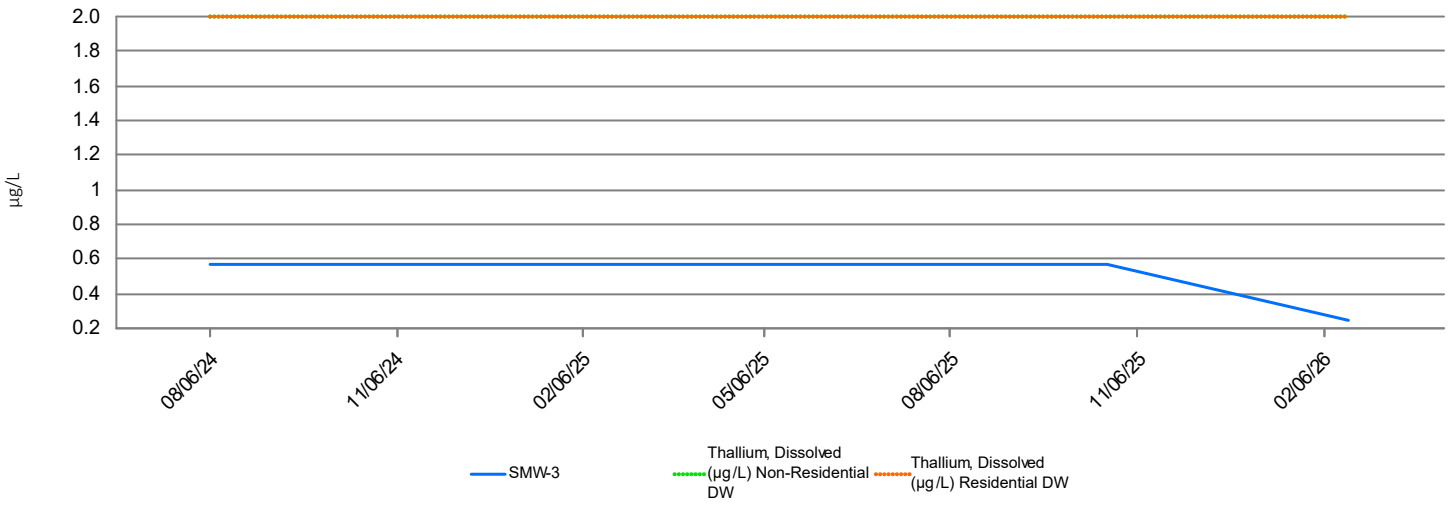
SMW-1



SMW-1SB



SMW-3



Printed Date: 05/21/2026

EHS DATA

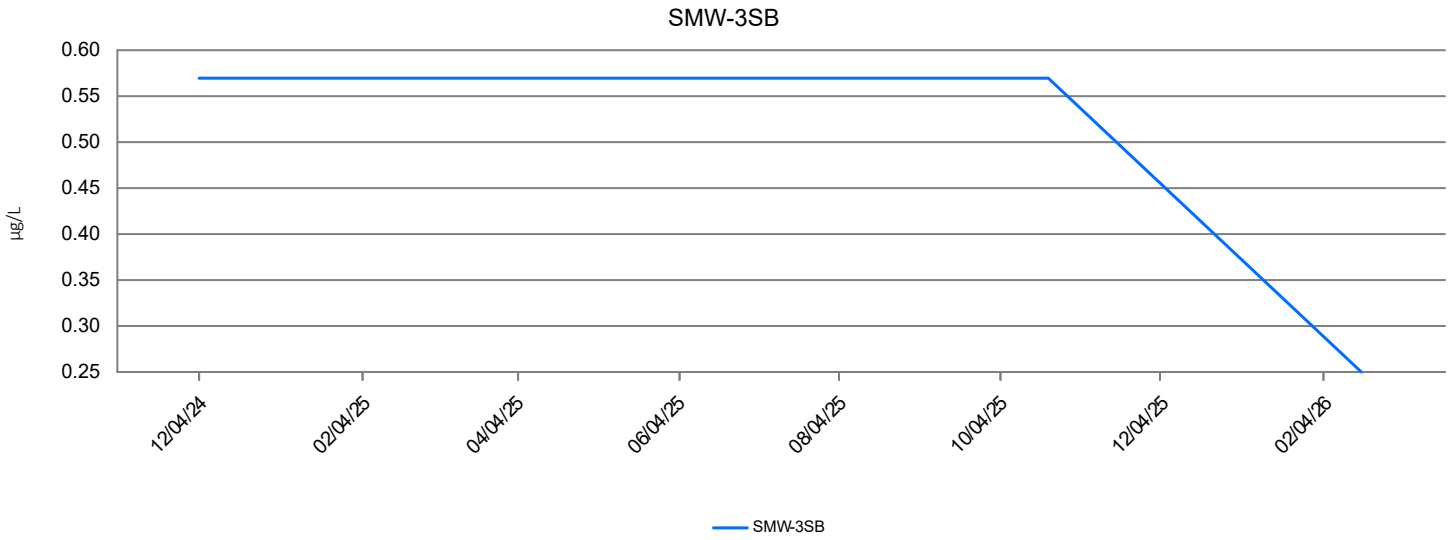
MCERTS Cert. no. Sira MC090140/02

MCERTS

Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

No Group Selected, Thallium, Dissolved (µg/L)

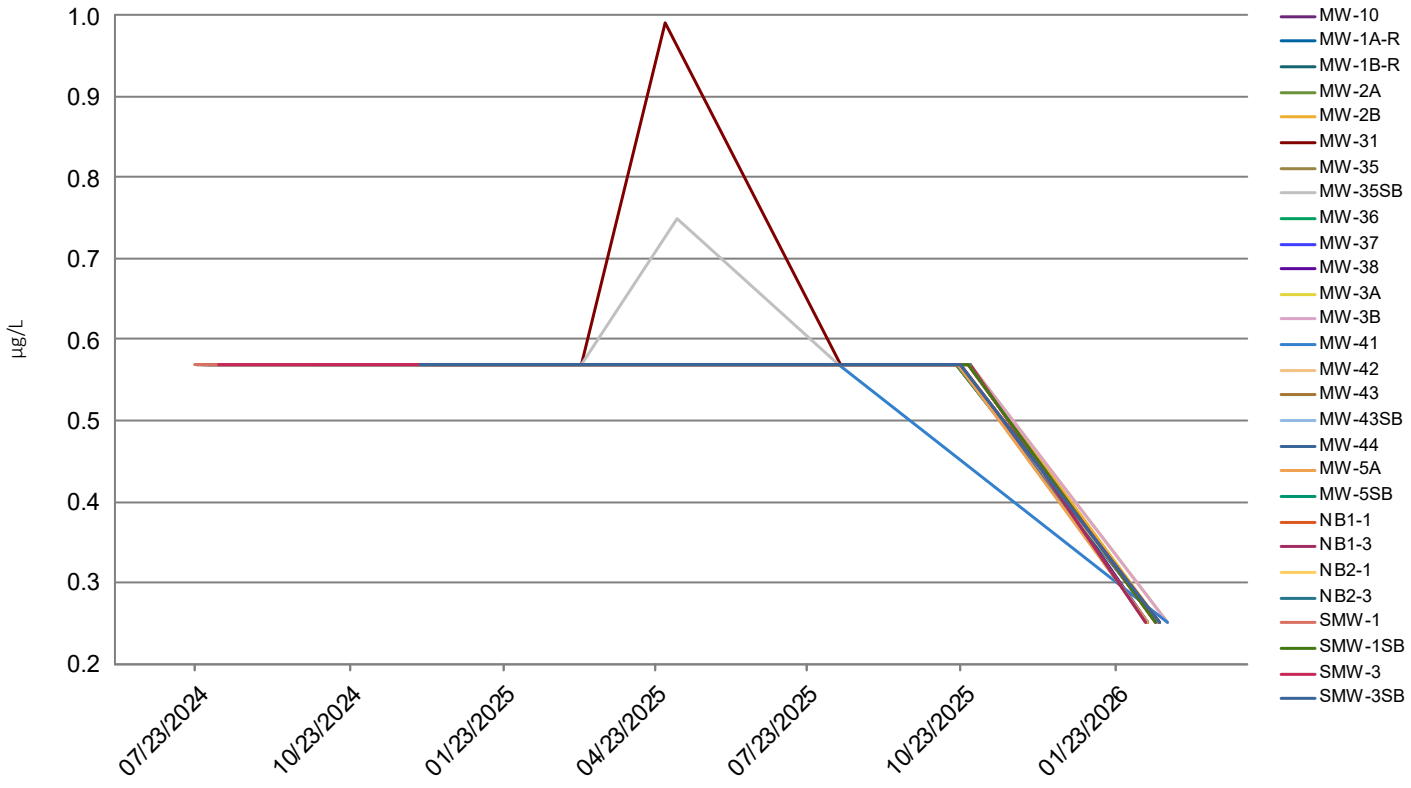


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Thallium, Total Recoverable (µg/L)



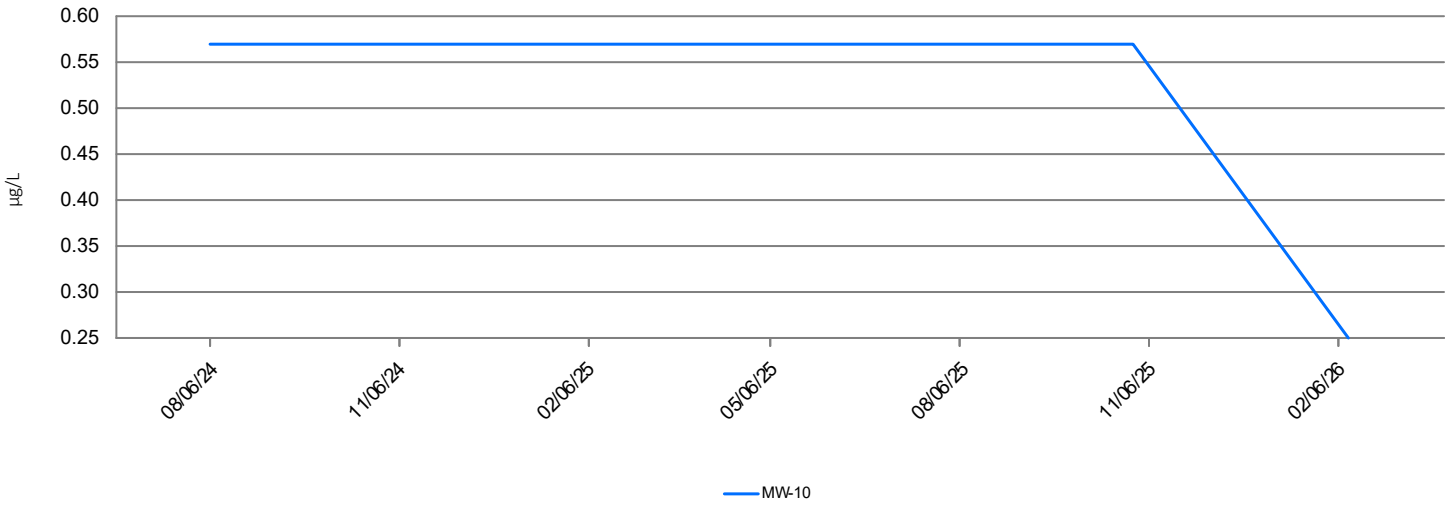
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

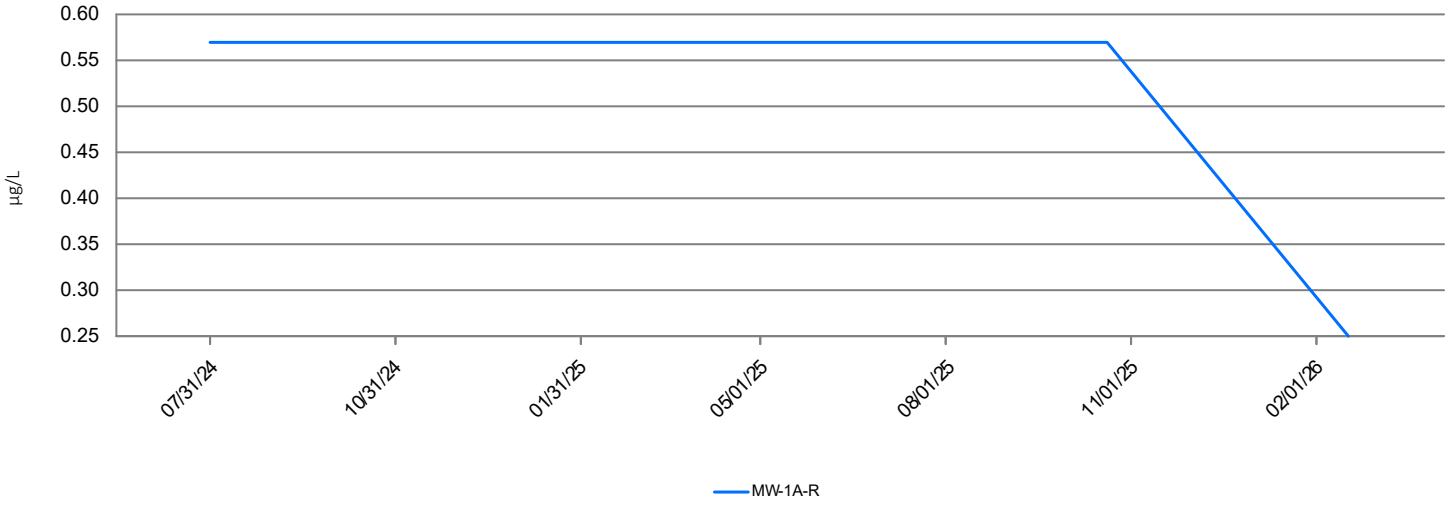
MonitorPro

No Group Selected, Thallium, Total Recoverable (µg/L)

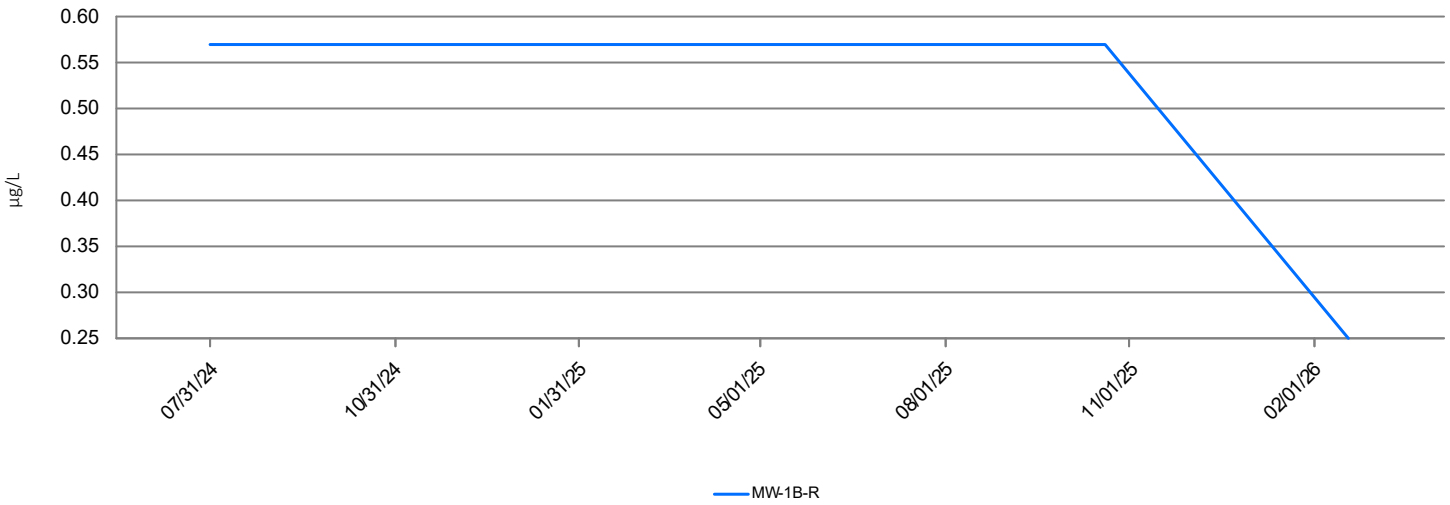
MW-10



MW-1A-R



MW-1B-R



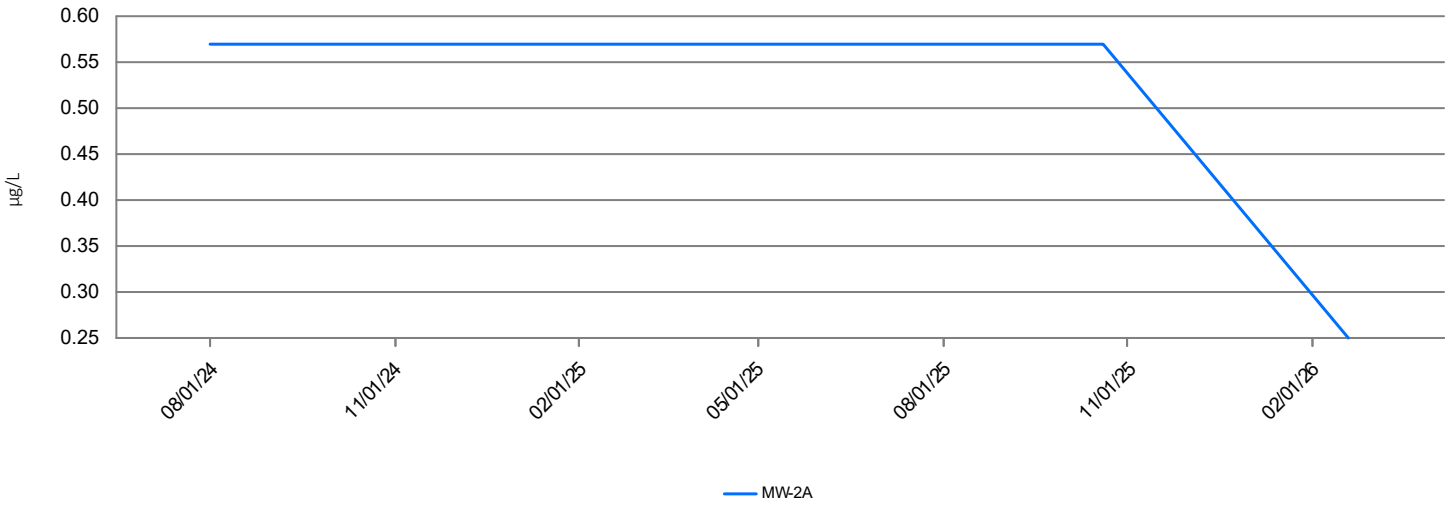
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

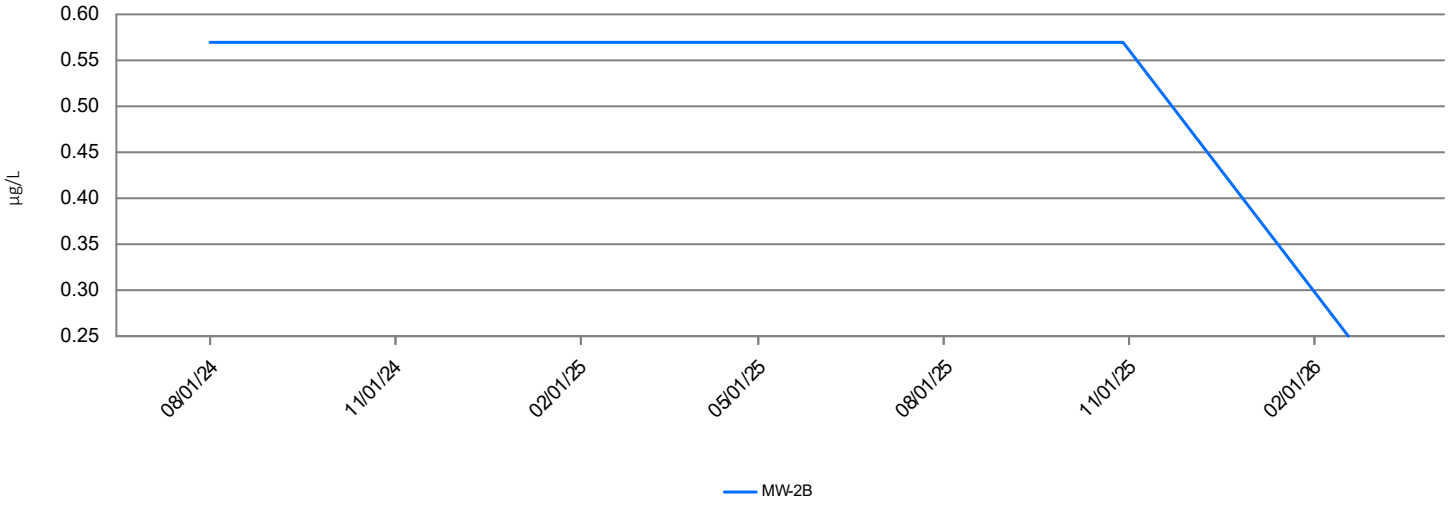
MonitorPro

No Group Selected, Thallium, Total Recoverable (µg/L)

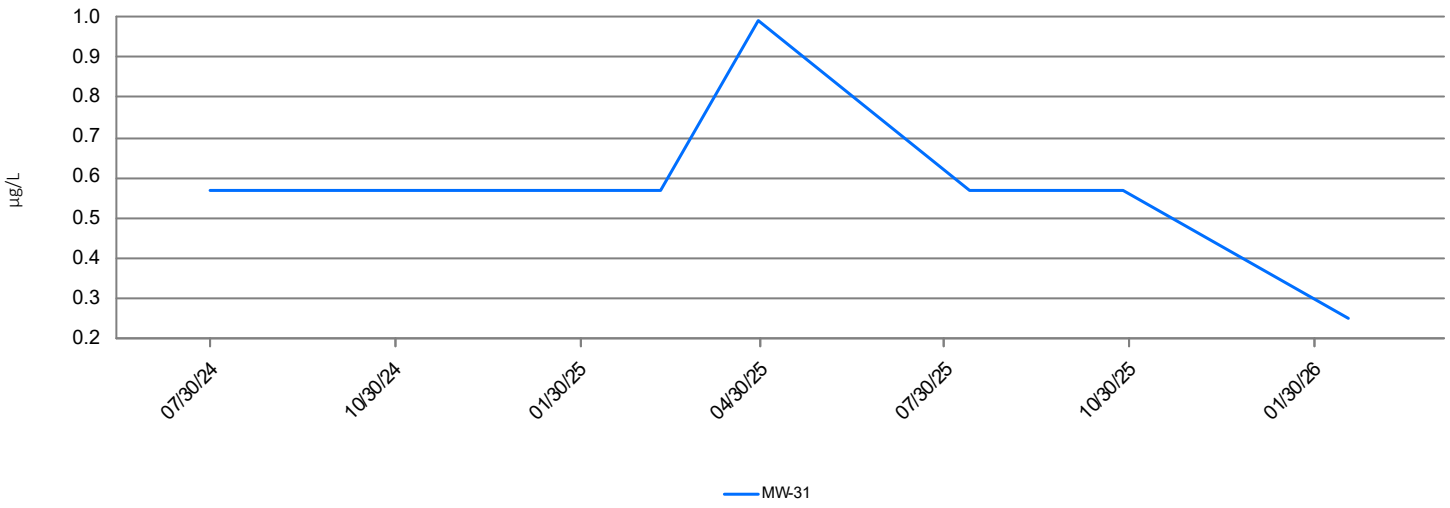
MW-2A



MW-2B



MW-31

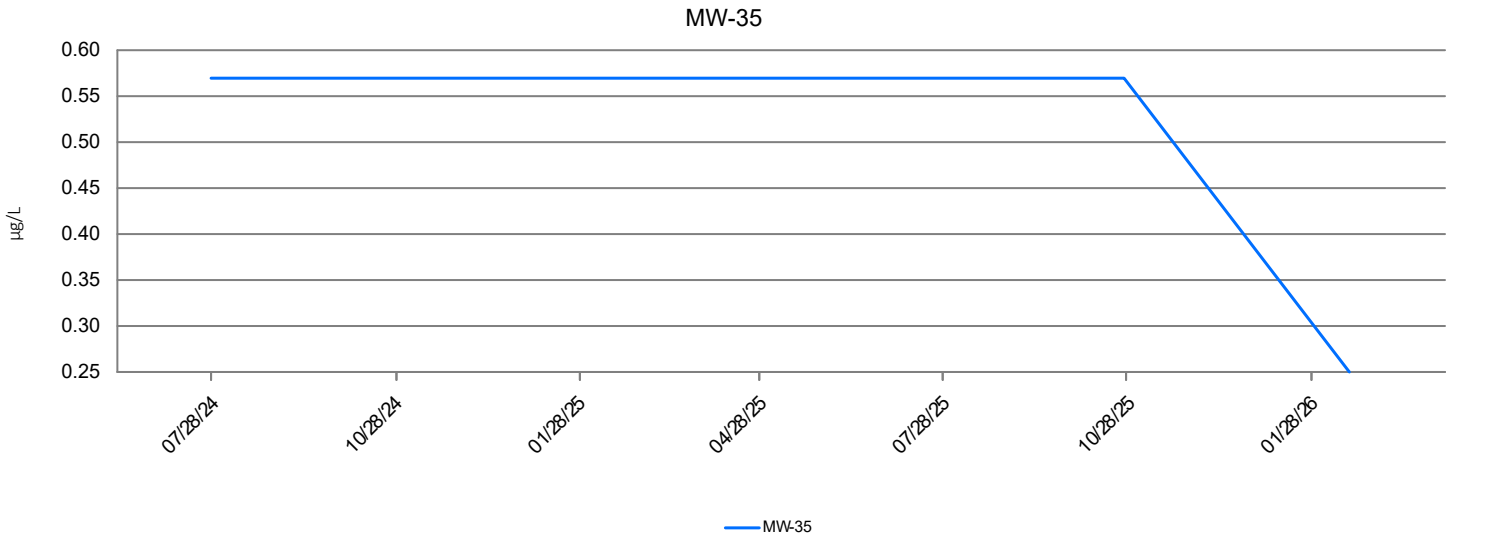


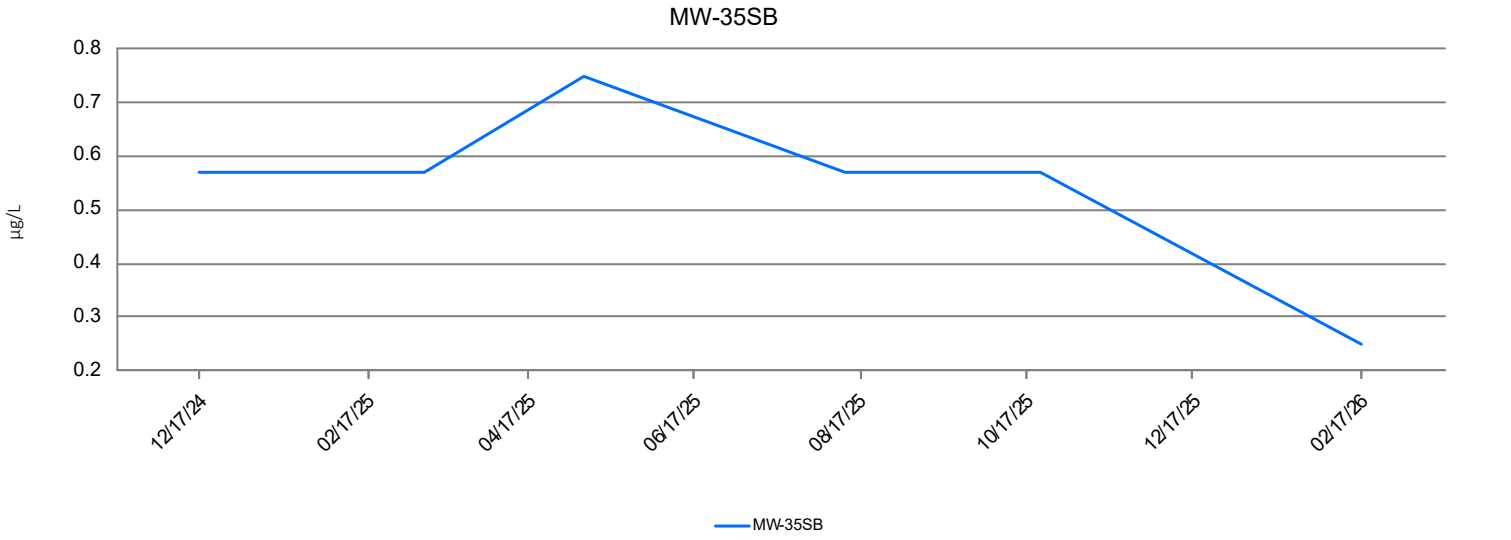
Variable Graphical Report

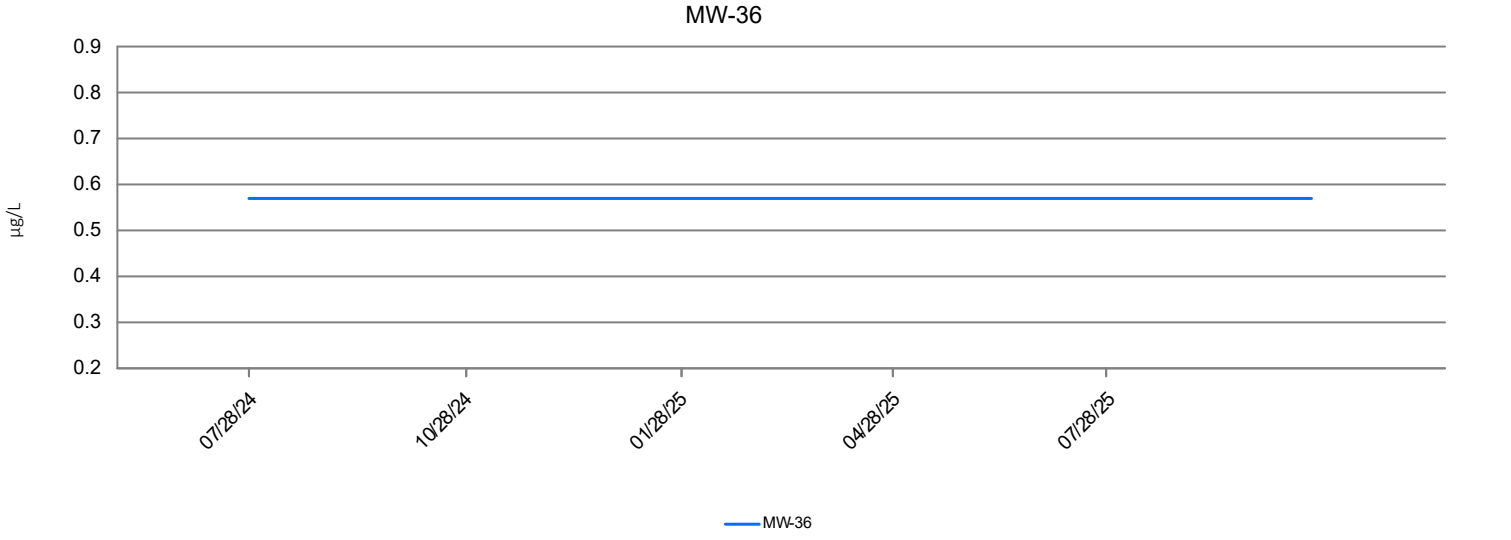
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Thallium, Total Recoverable (µg/L)





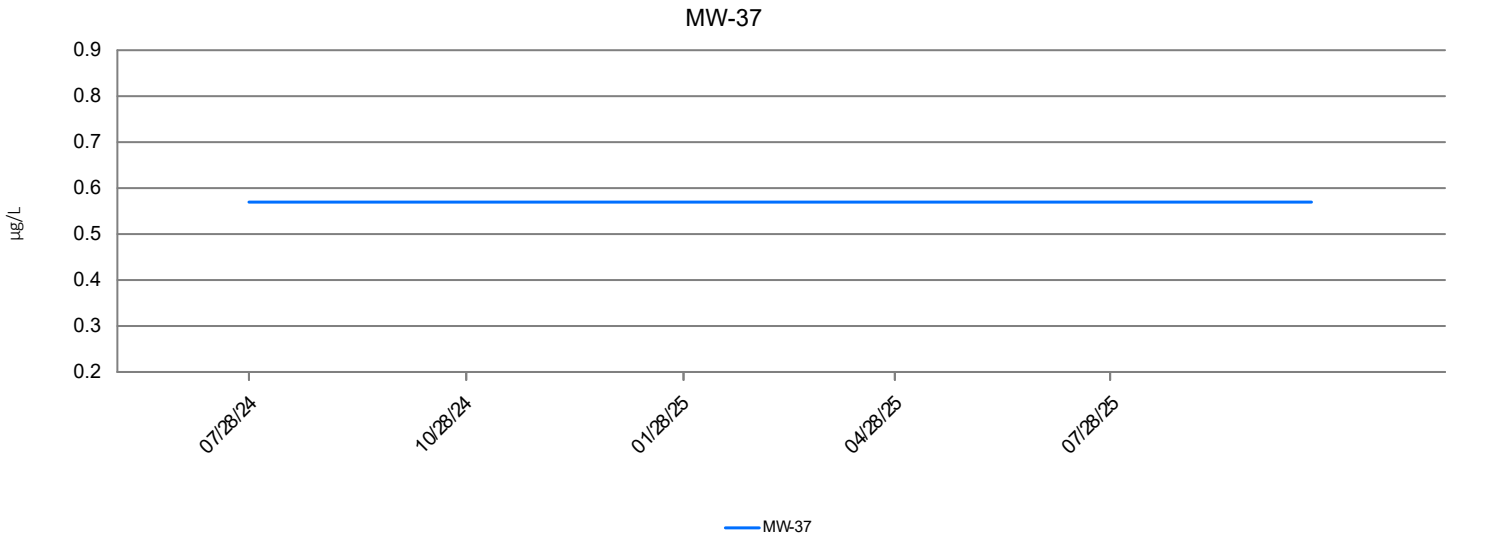


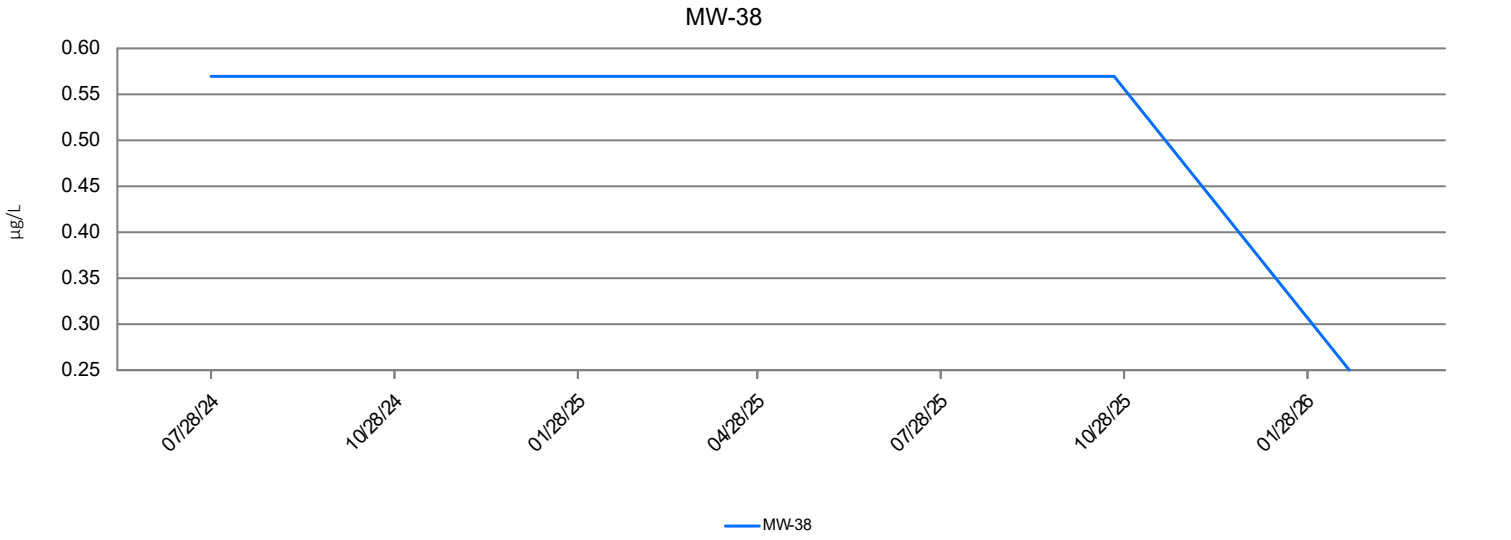
Variable Graphical Report

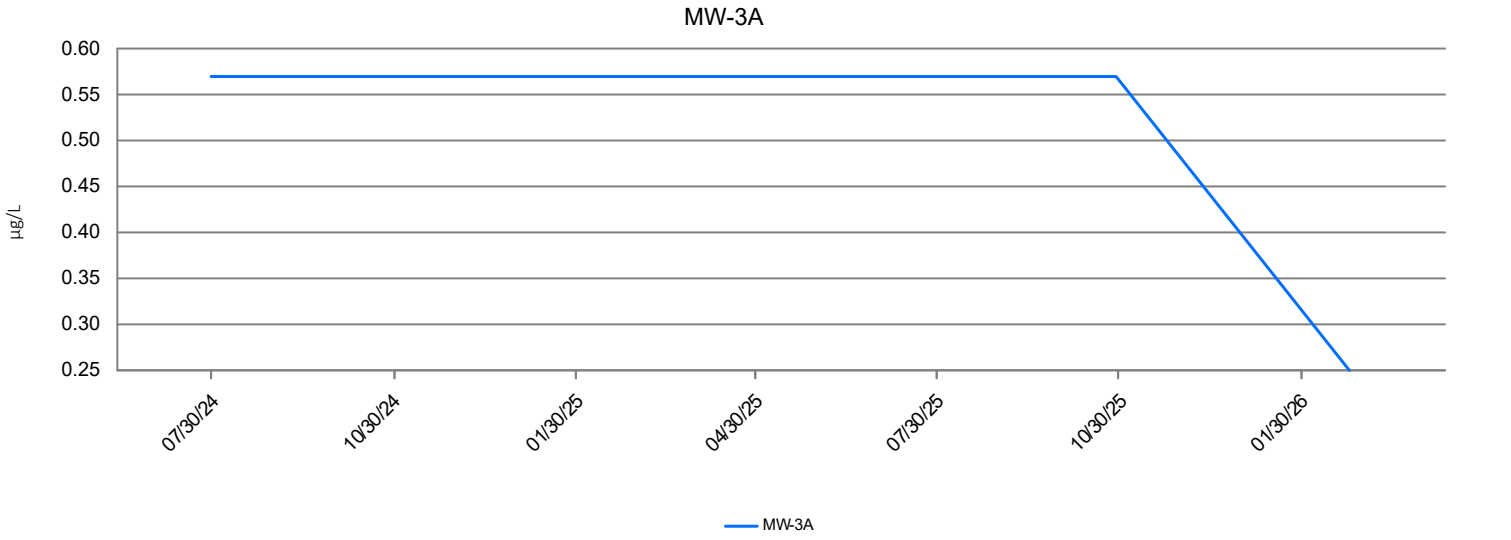
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Thallium, Total Recoverable (µg/L)







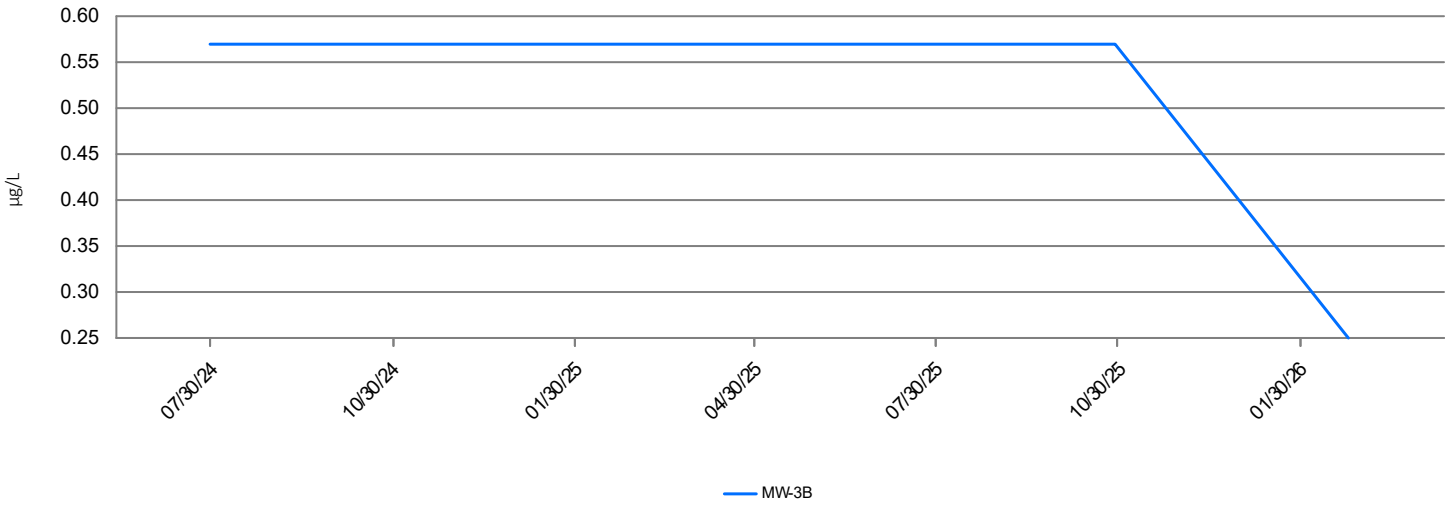
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

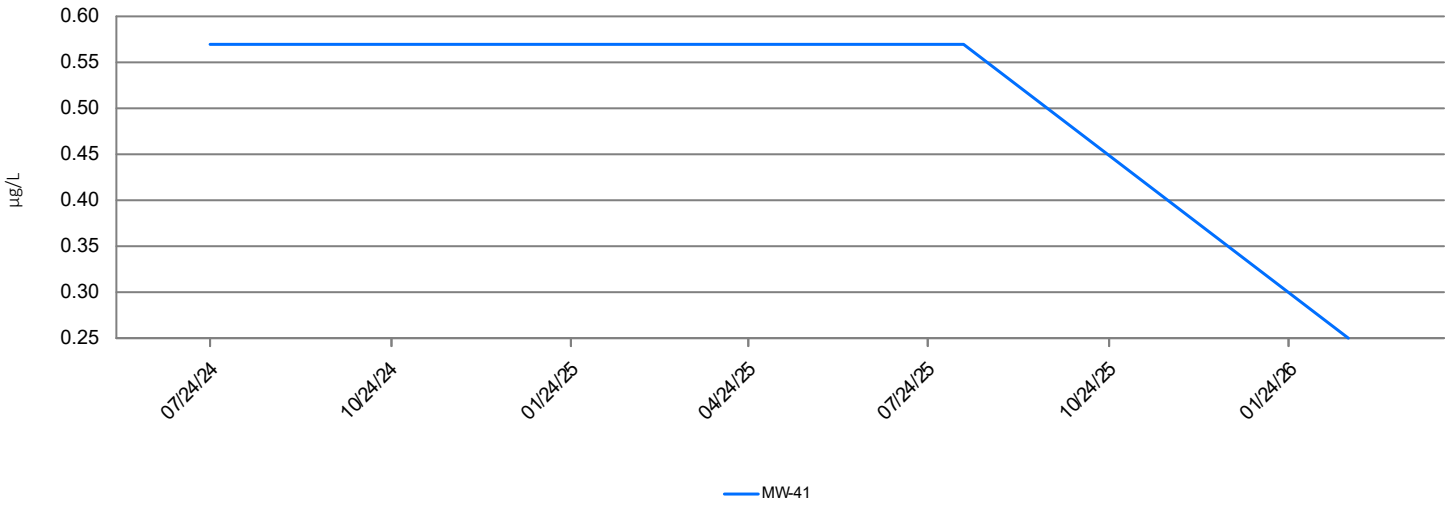
MonitorPro

No Group Selected, Thallium, Total Recoverable (µg/L)

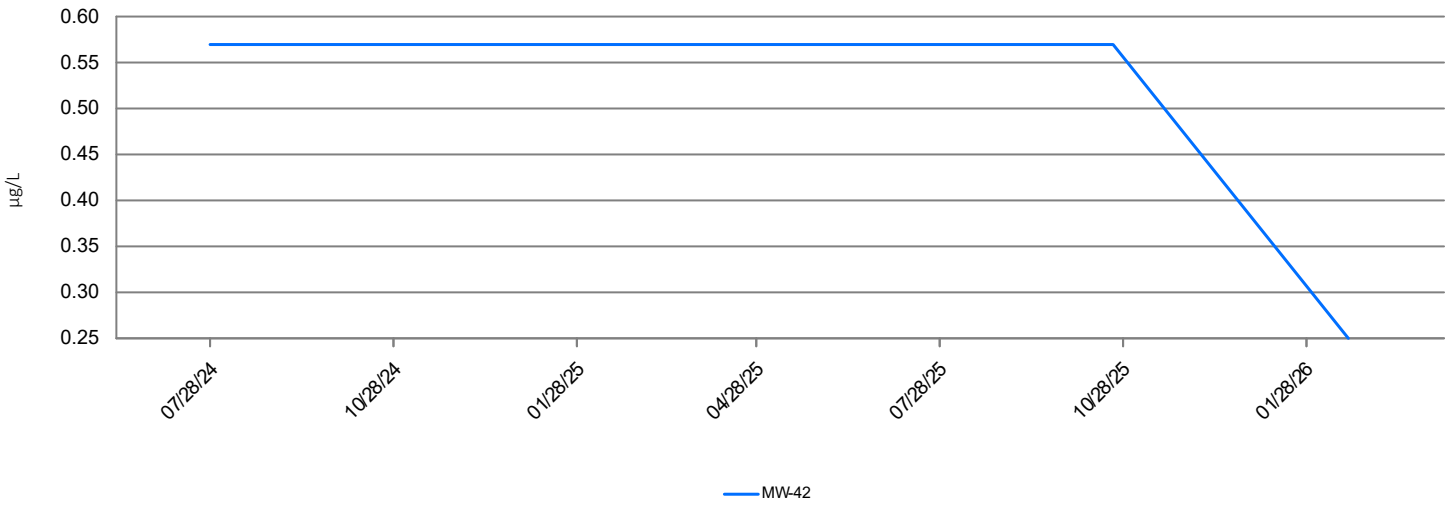
MW-3B



MW-41



MW-42



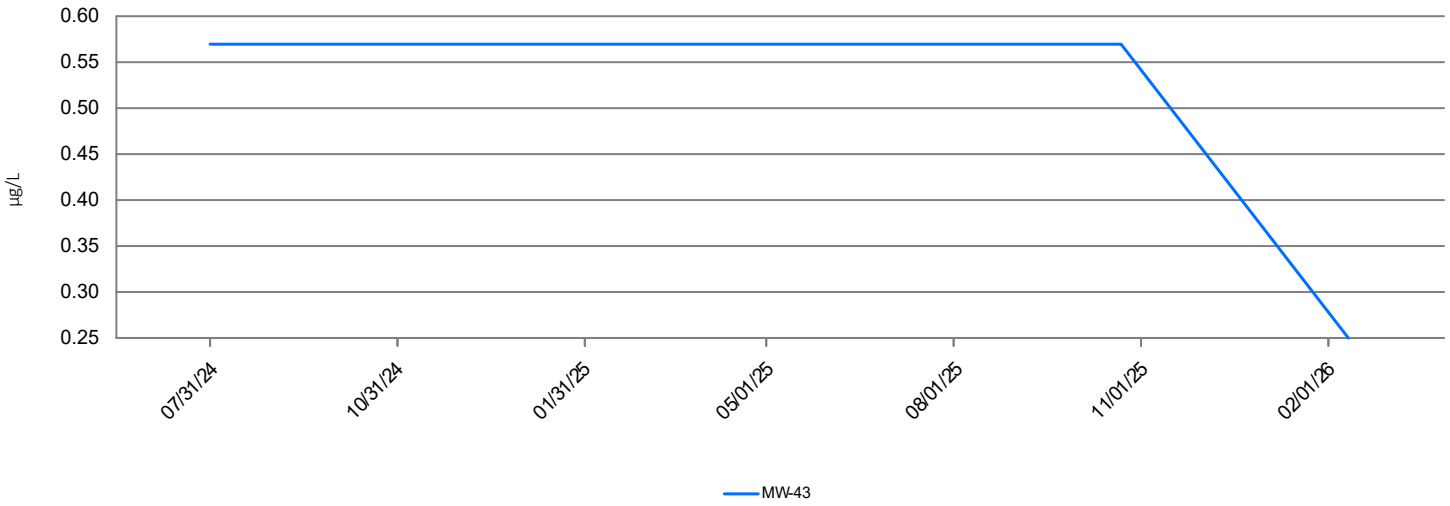
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

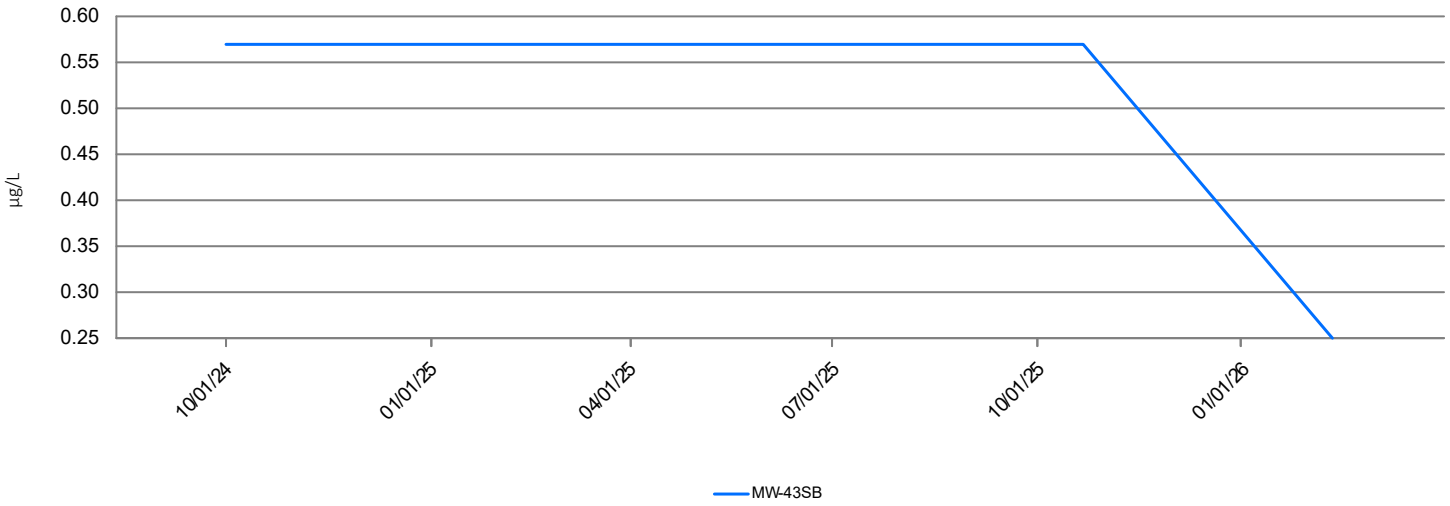
MonitorPro

No Group Selected, Thallium, Total Recoverable (µg/L)

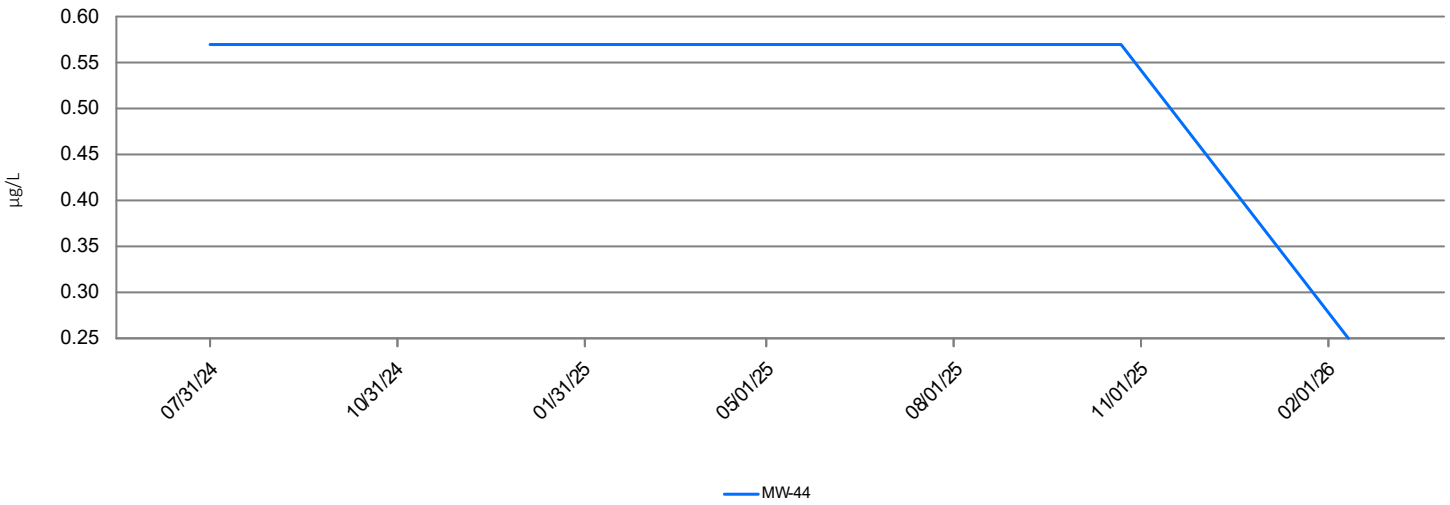
MW-43



MW-43SB



MW-44

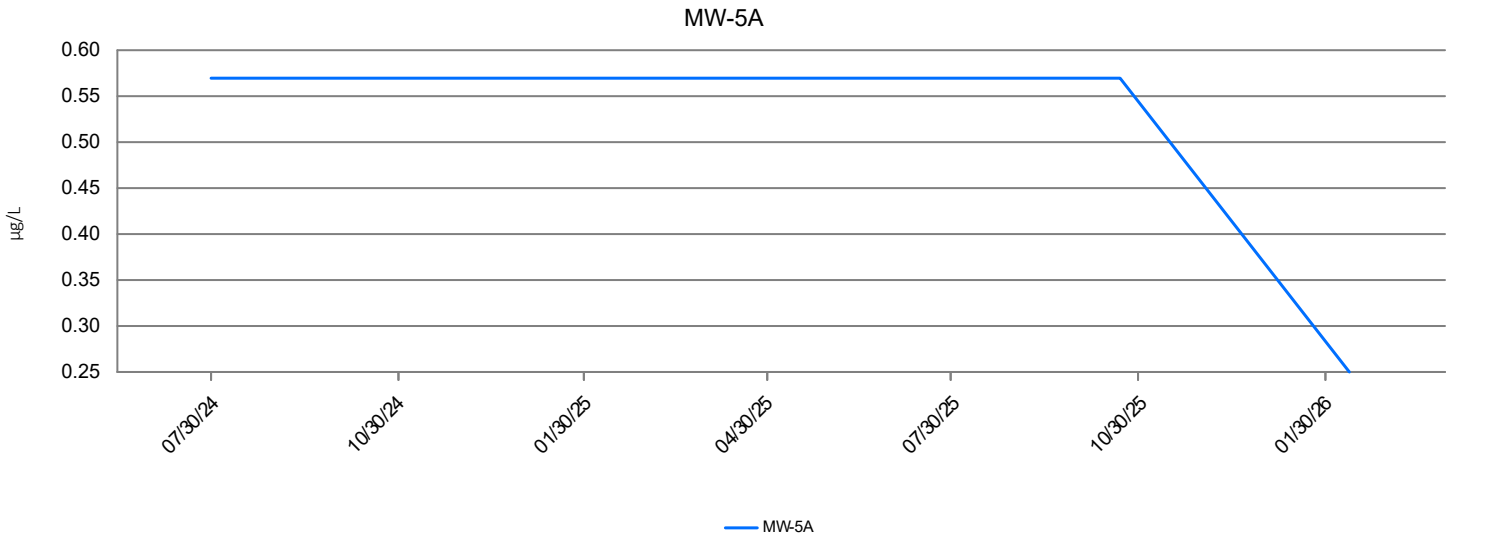


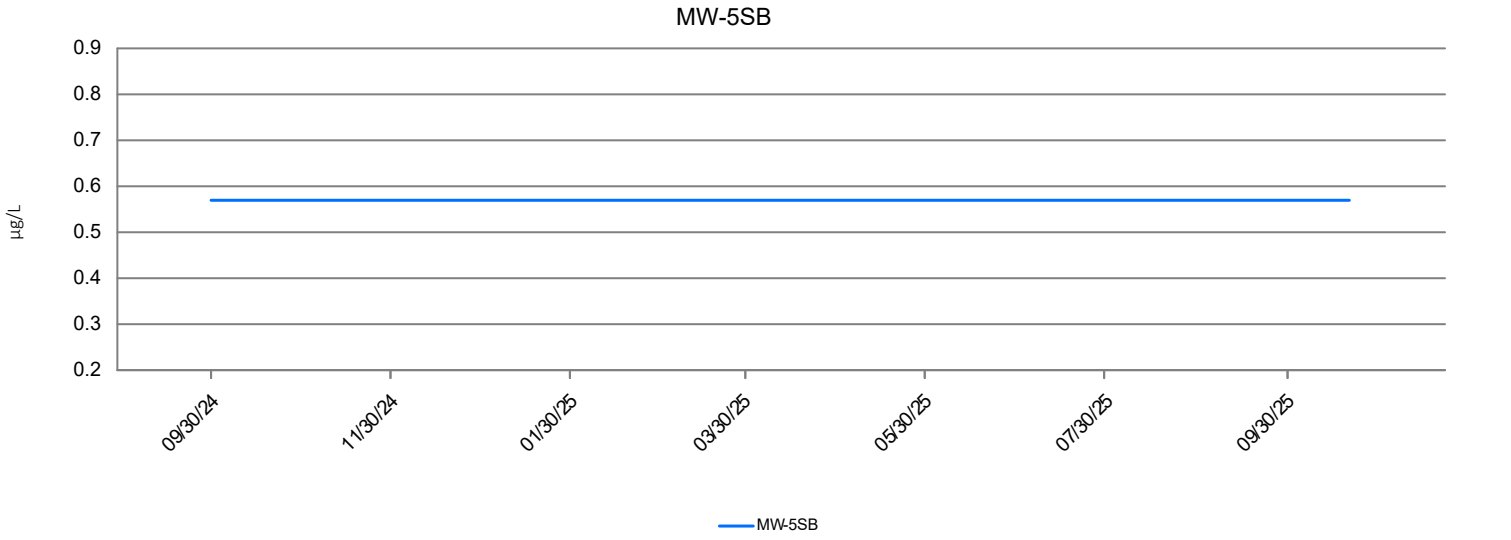
Variable Graphical Report

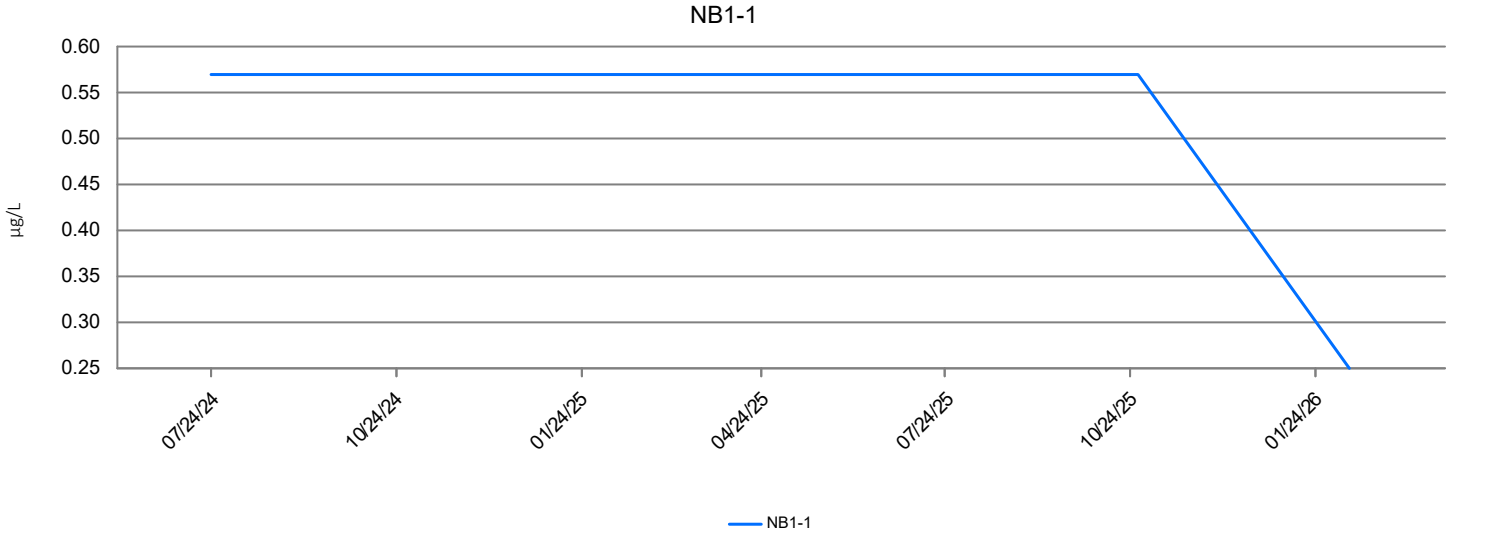
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Thallium, Total Recoverable (µg/L)







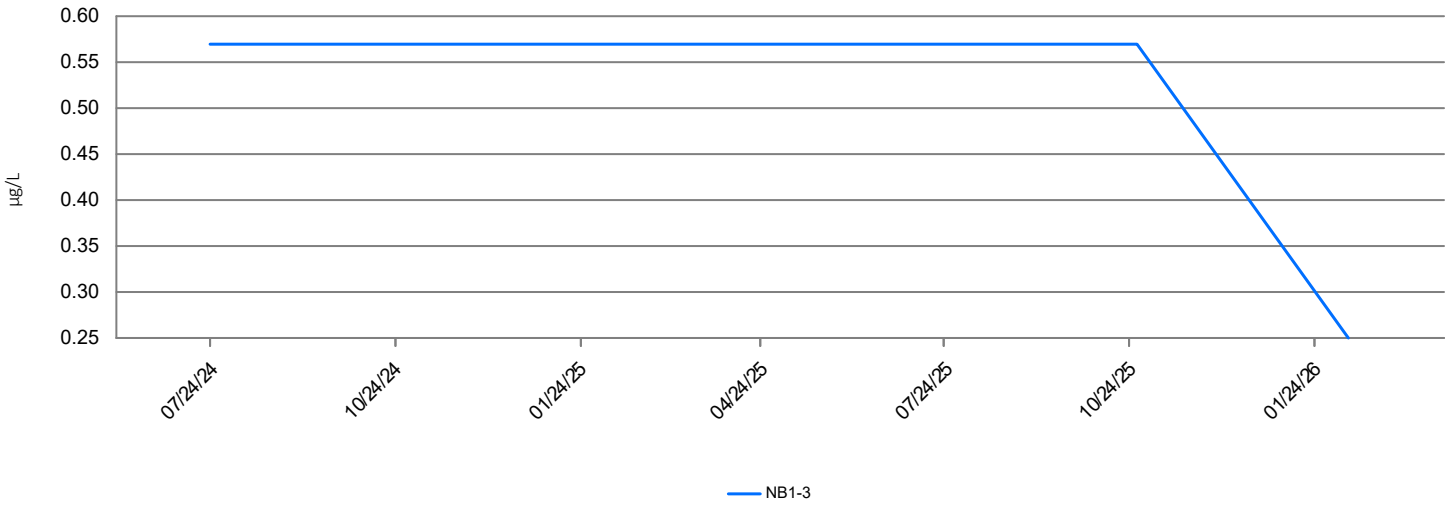
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

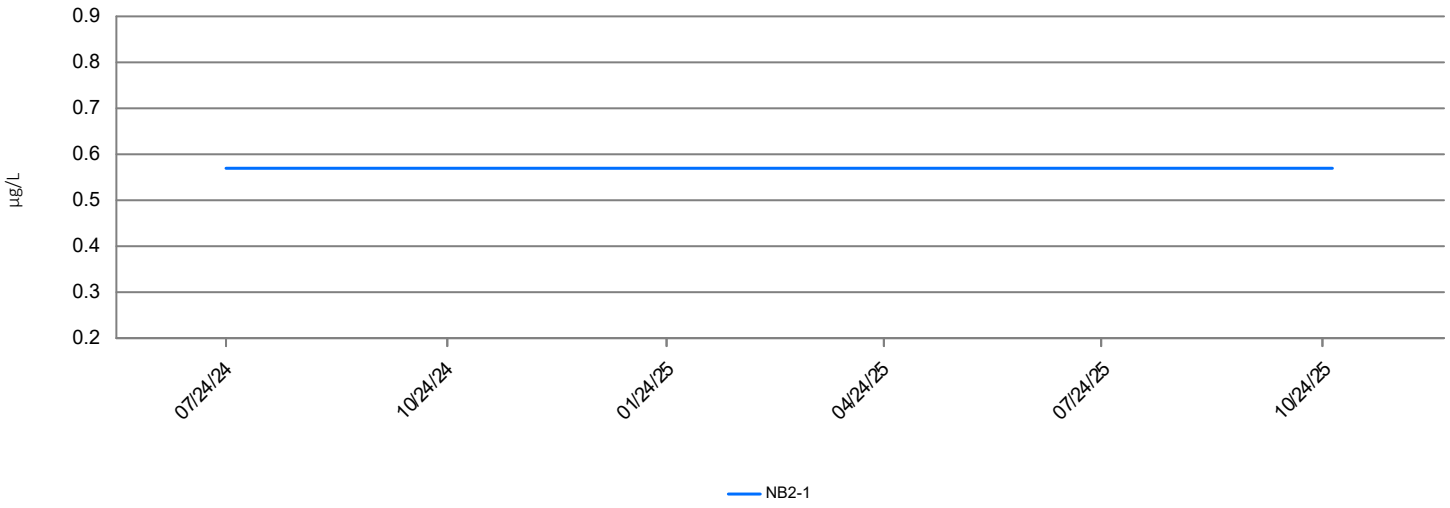
MonitorPro

No Group Selected, Thallium, Total Recoverable (µg/L)

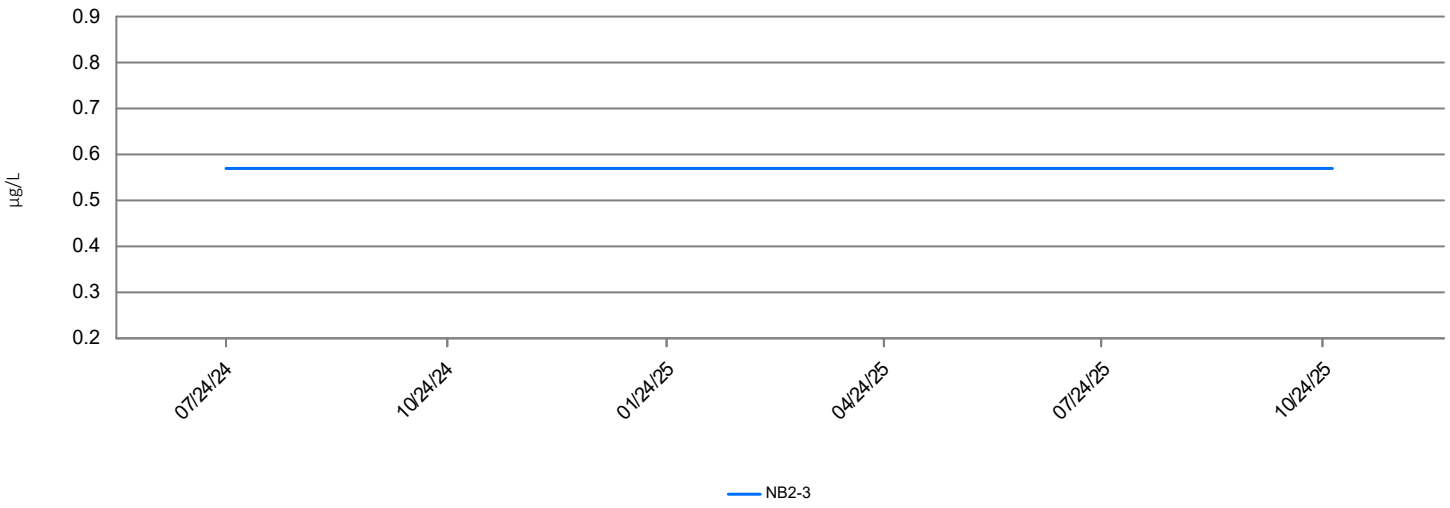
NB1-3



NB2-1



NB2-3



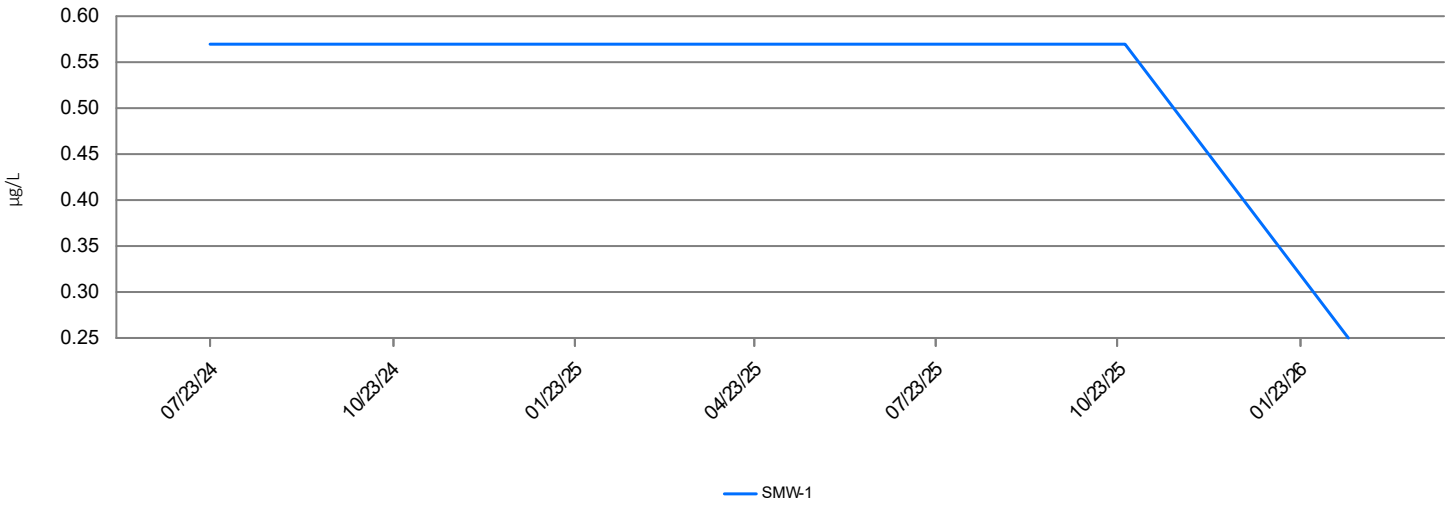
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

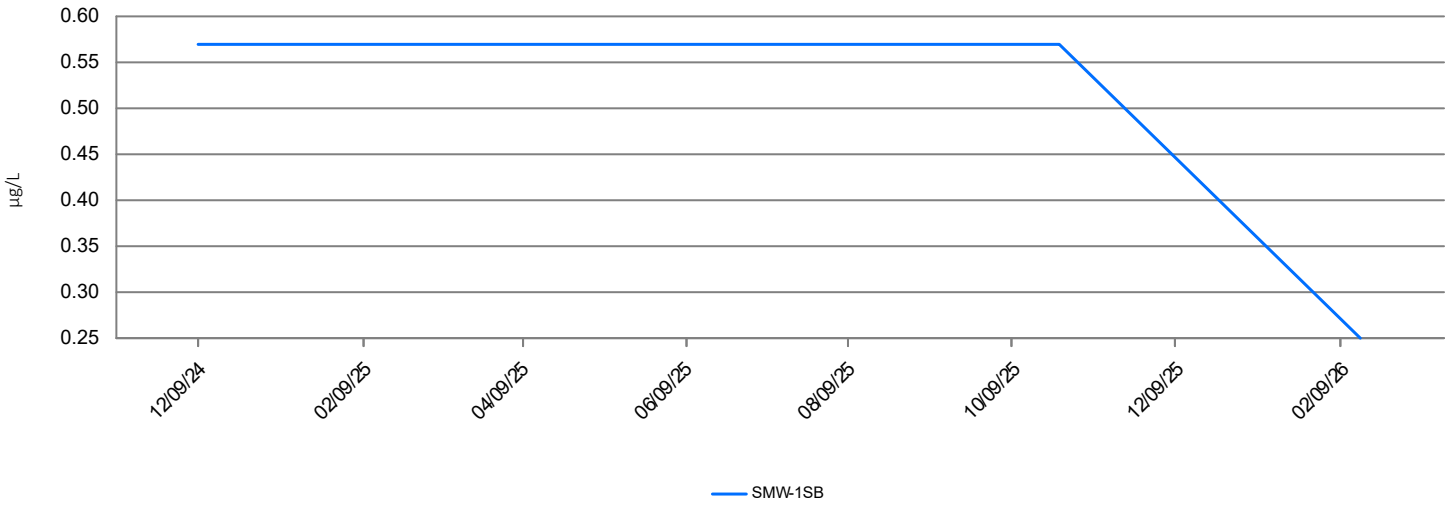
MonitorPro

No Group Selected, Thallium, Total Recoverable (µg/L)

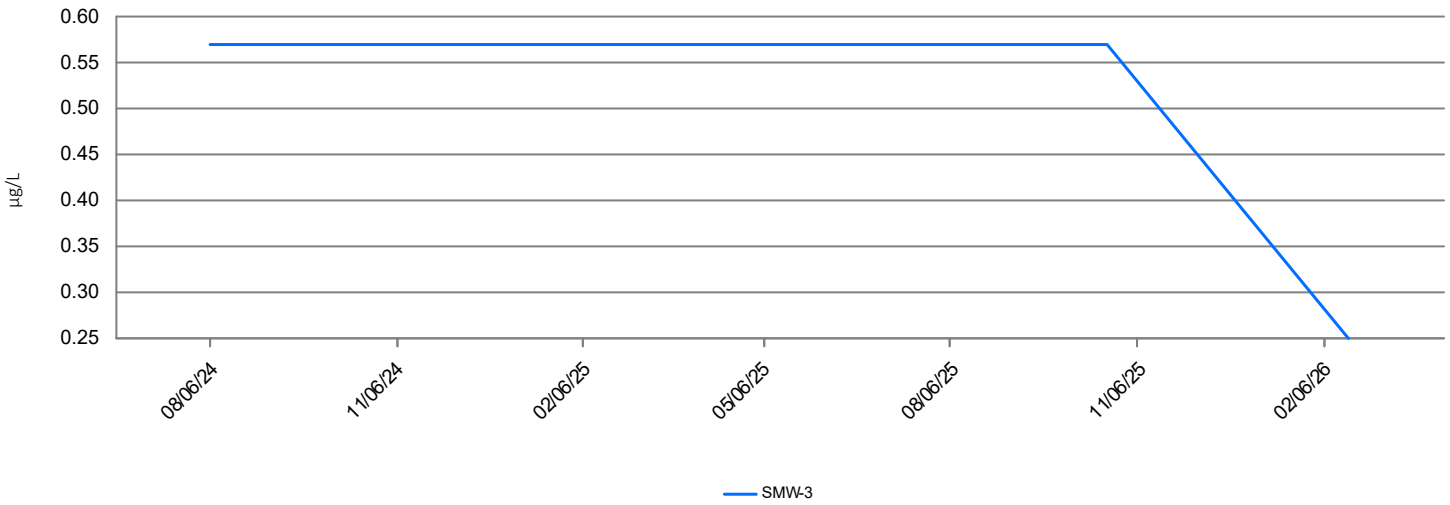
SMW-1



SMW-1SB



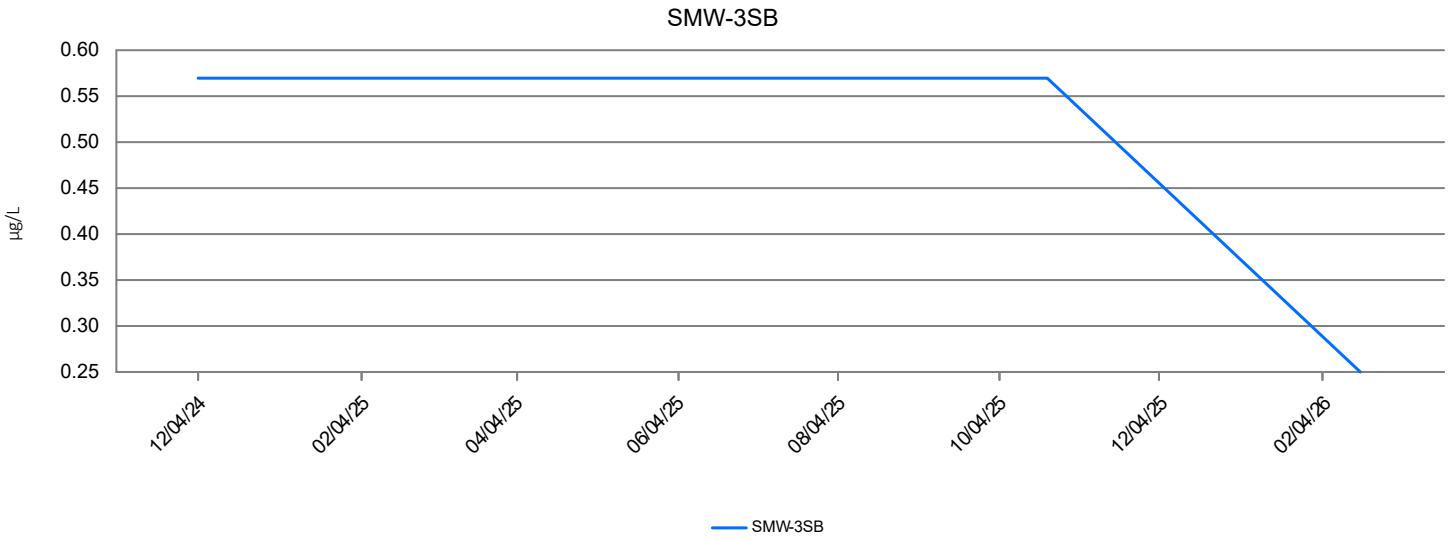
SMW-3



Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

No Group Selected, Thallium, Total Recoverable (µg/L)

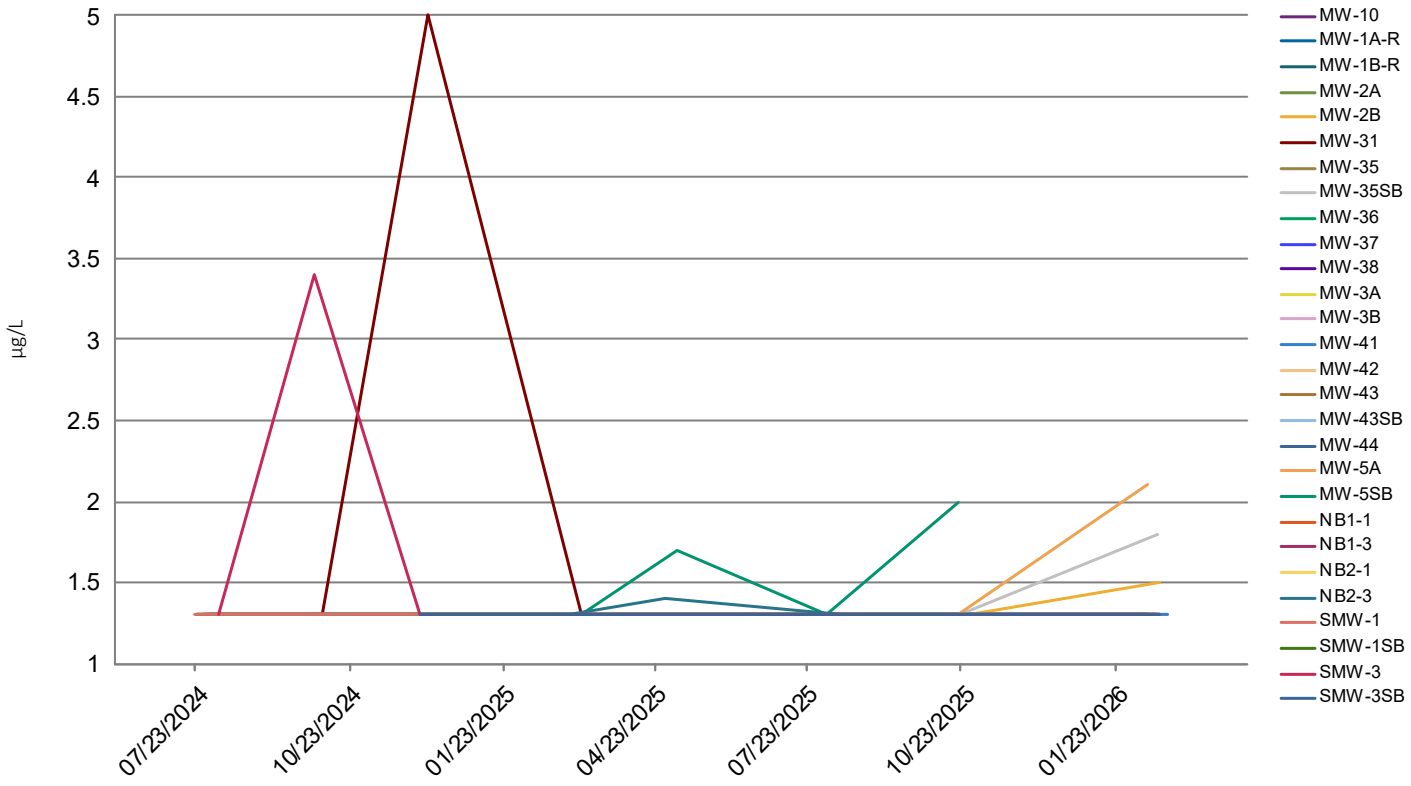


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Tin, Dissolved (µg/L)



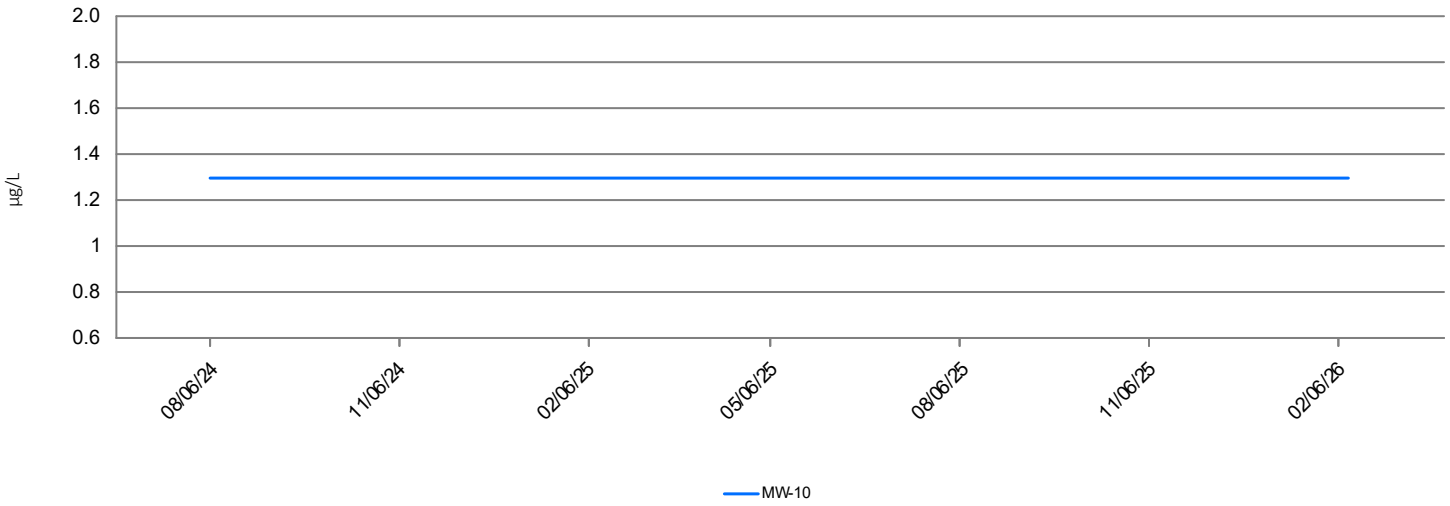
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

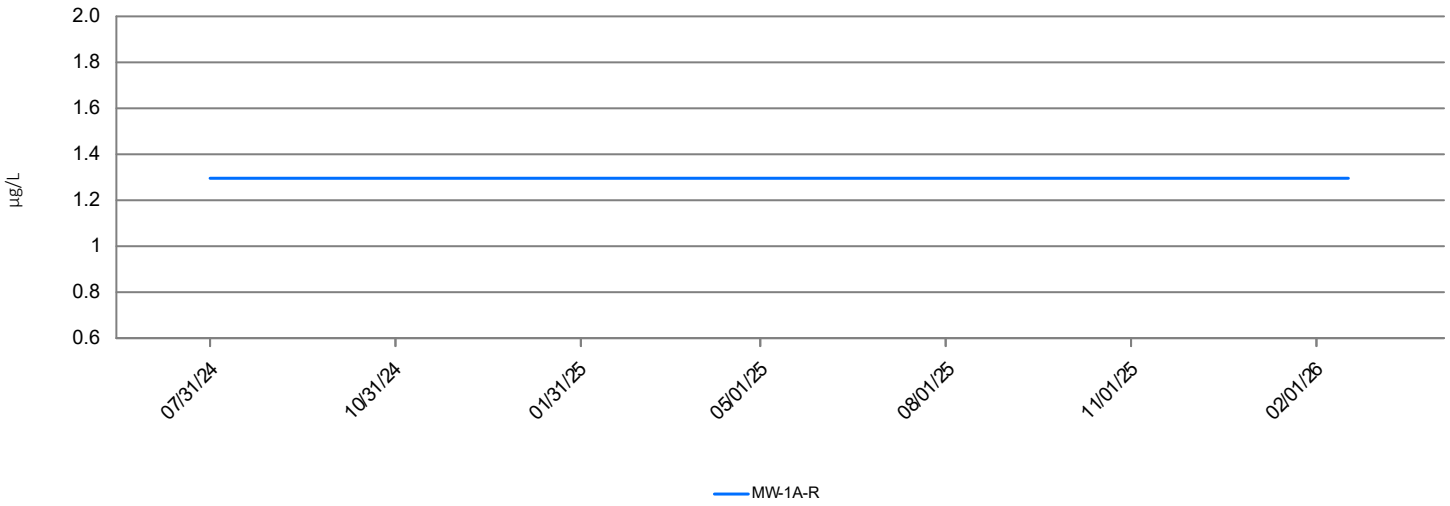
MonitorPro

No Group Selected, Tin, Dissolved (µg/L)

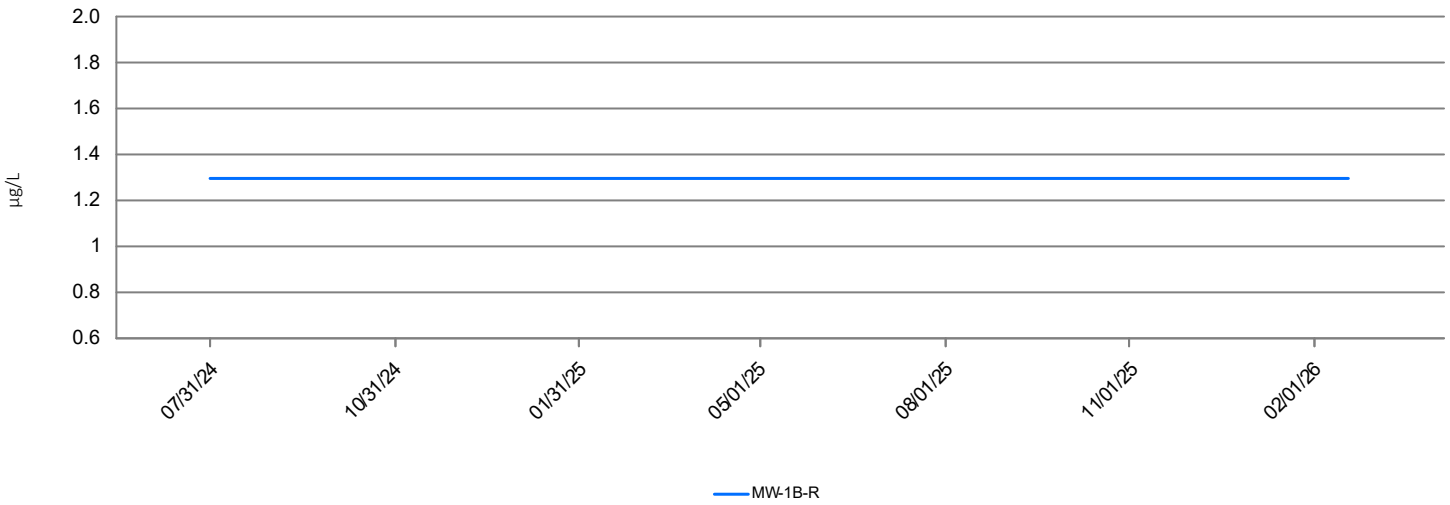
MW-10



MW-1A-R



MW-1B-R



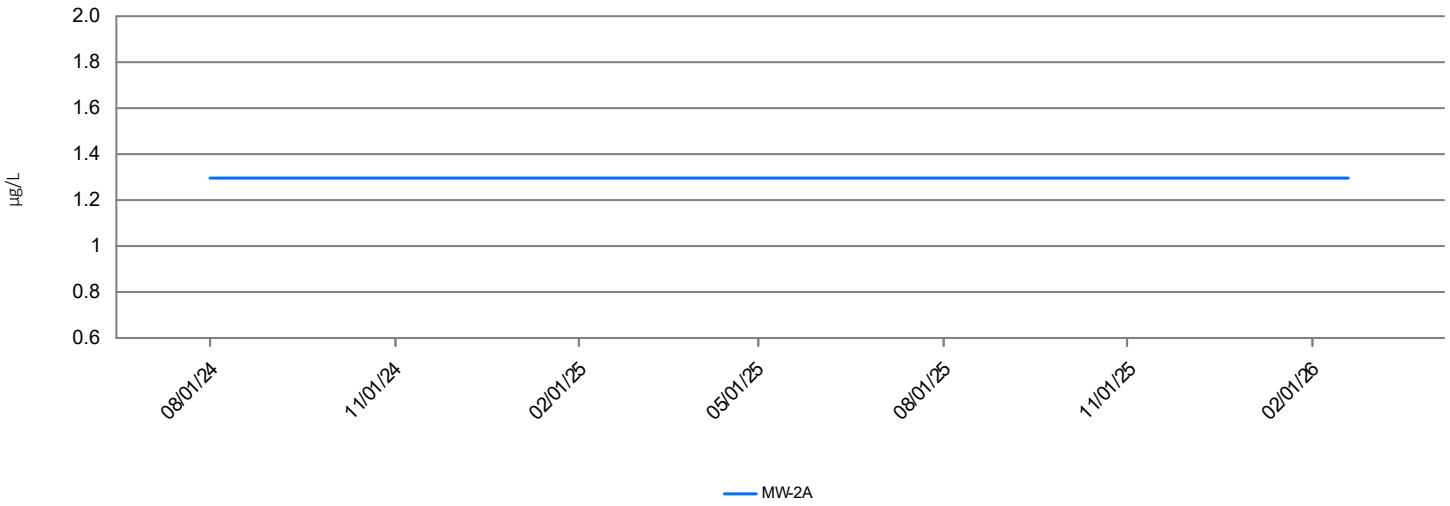
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

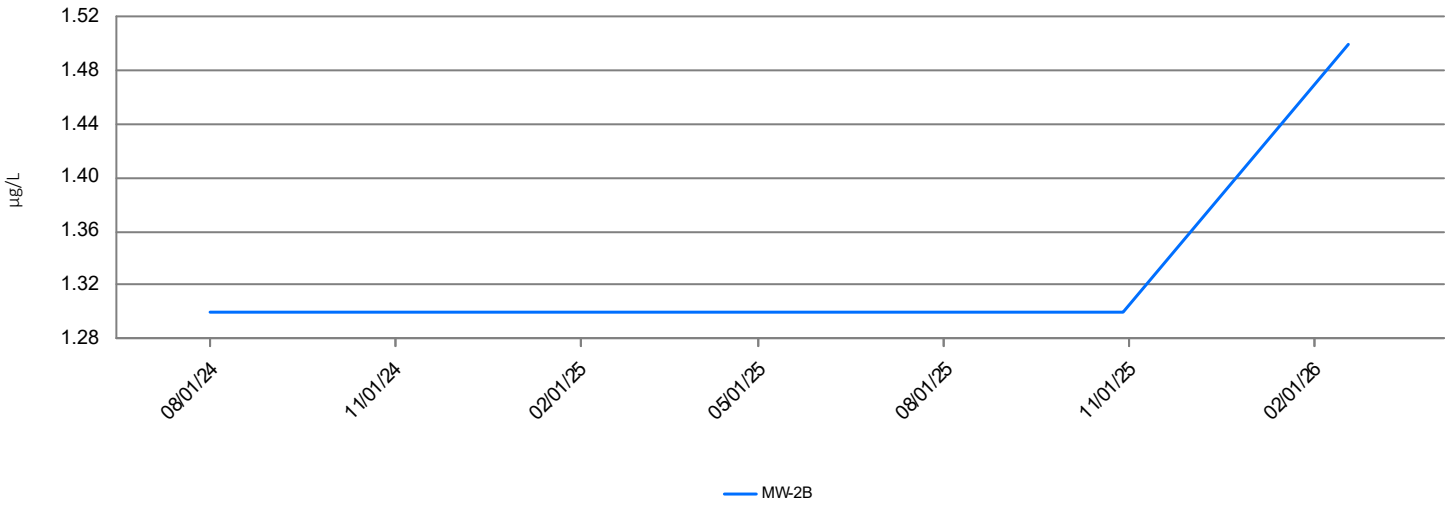
MonitorPro

No Group Selected, Tin, Dissolved (µg/L)

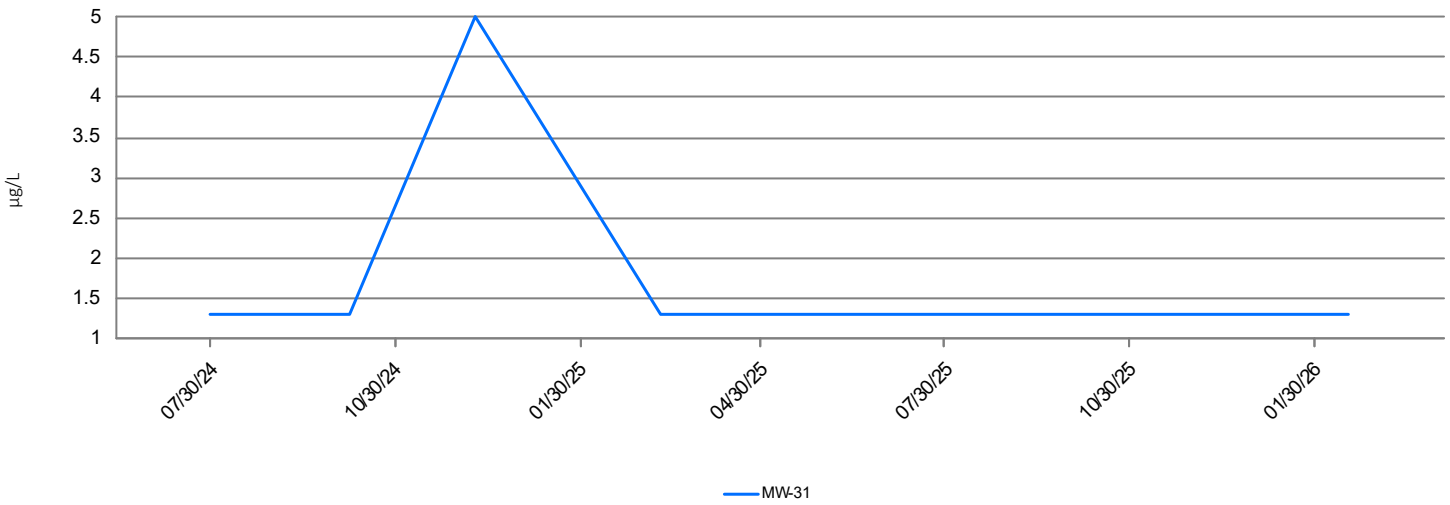
MW-2A



MW-2B



MW-31

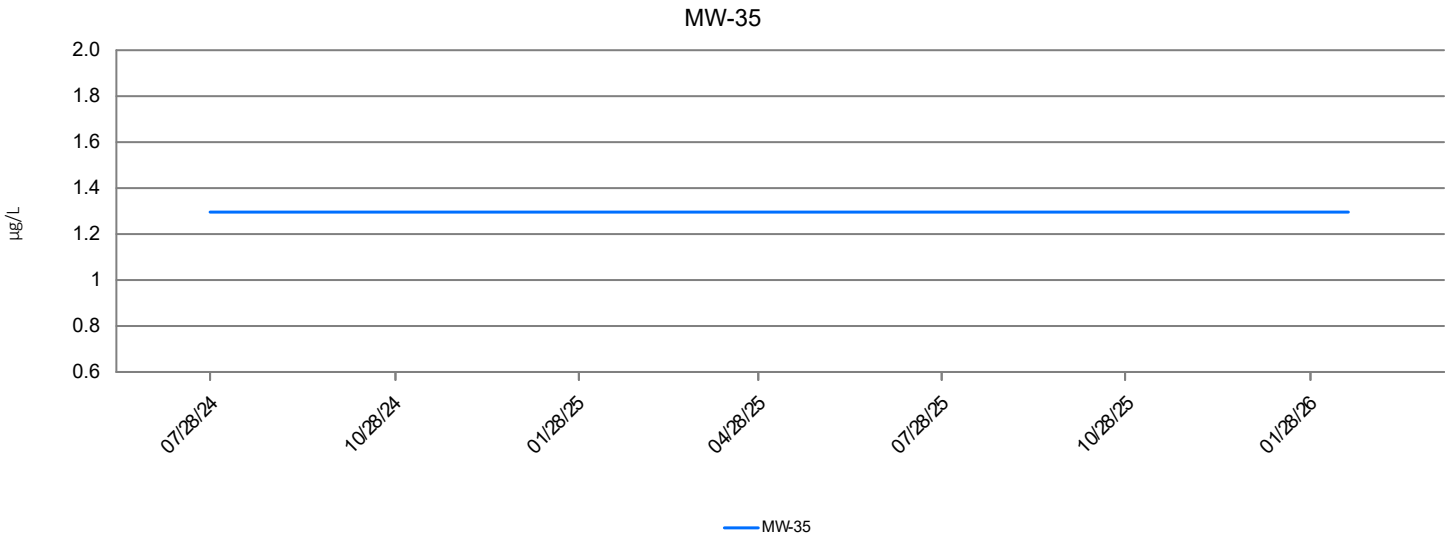


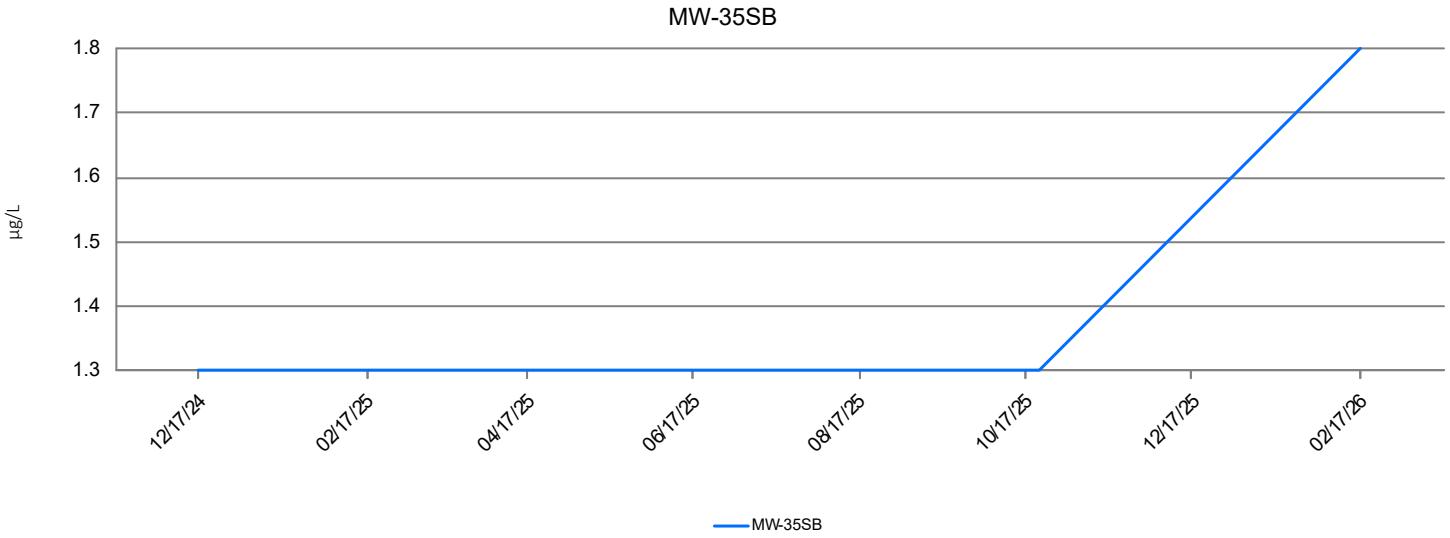
Variable Graphical Report

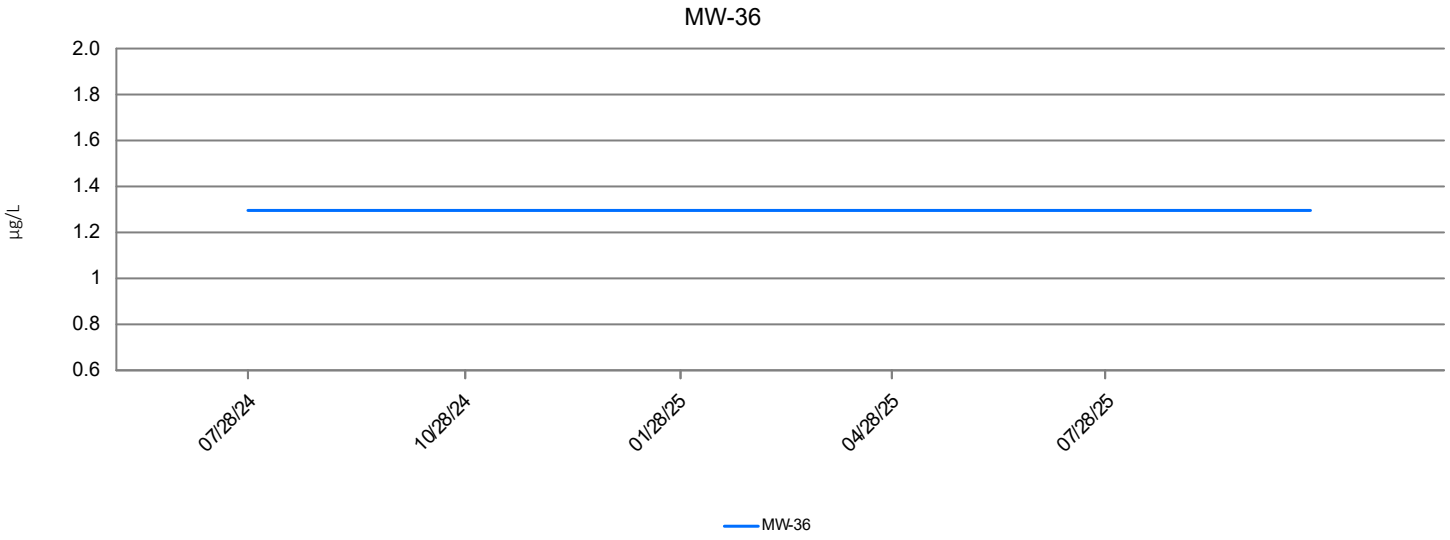
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Tin, Dissolved (µg/L)







Printed Date: 05/21/2026

EHS DATA

MCERTS Cert. no. Sira MC090140/02

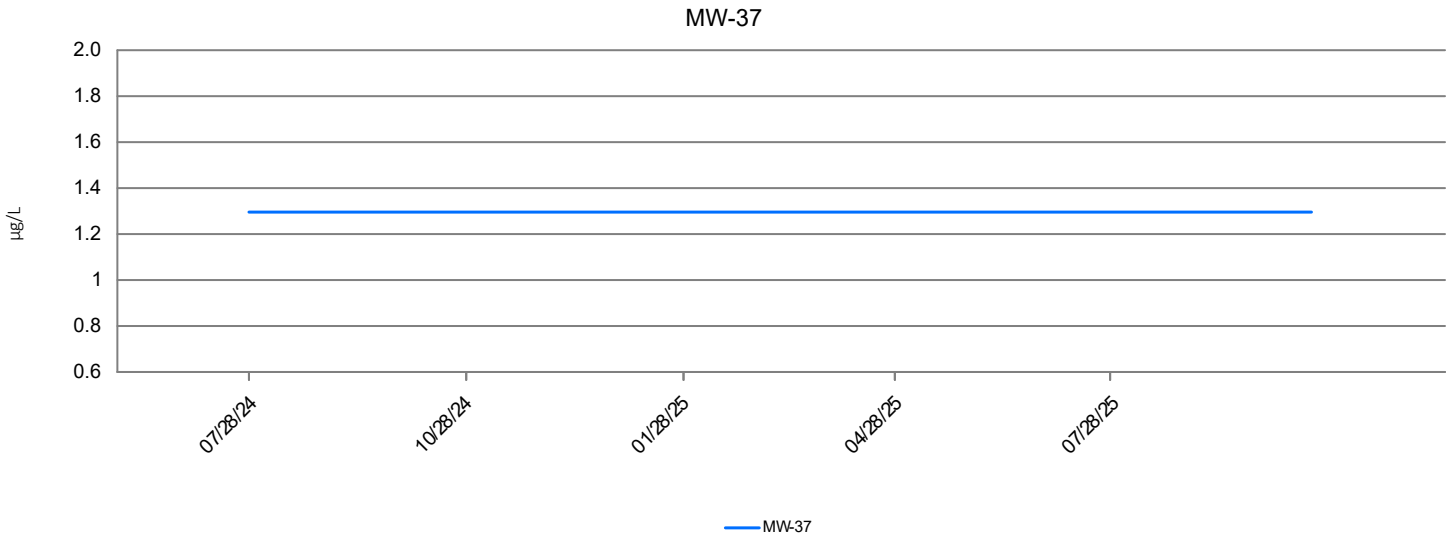
MCERTS

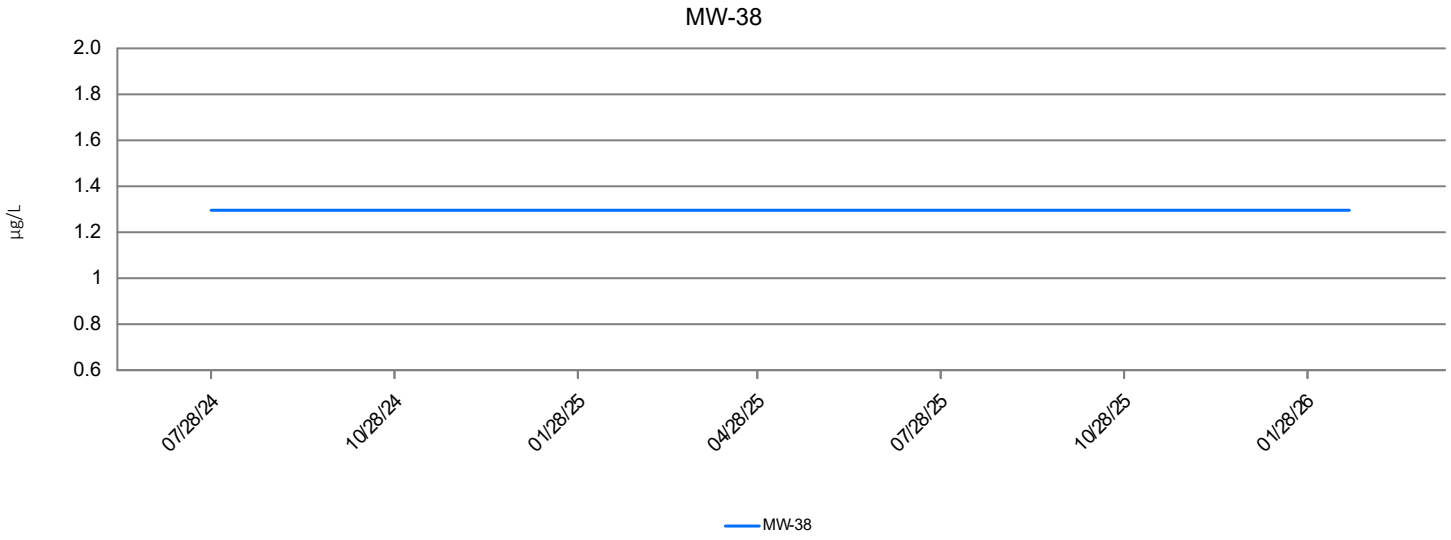
Variable Graphical Report

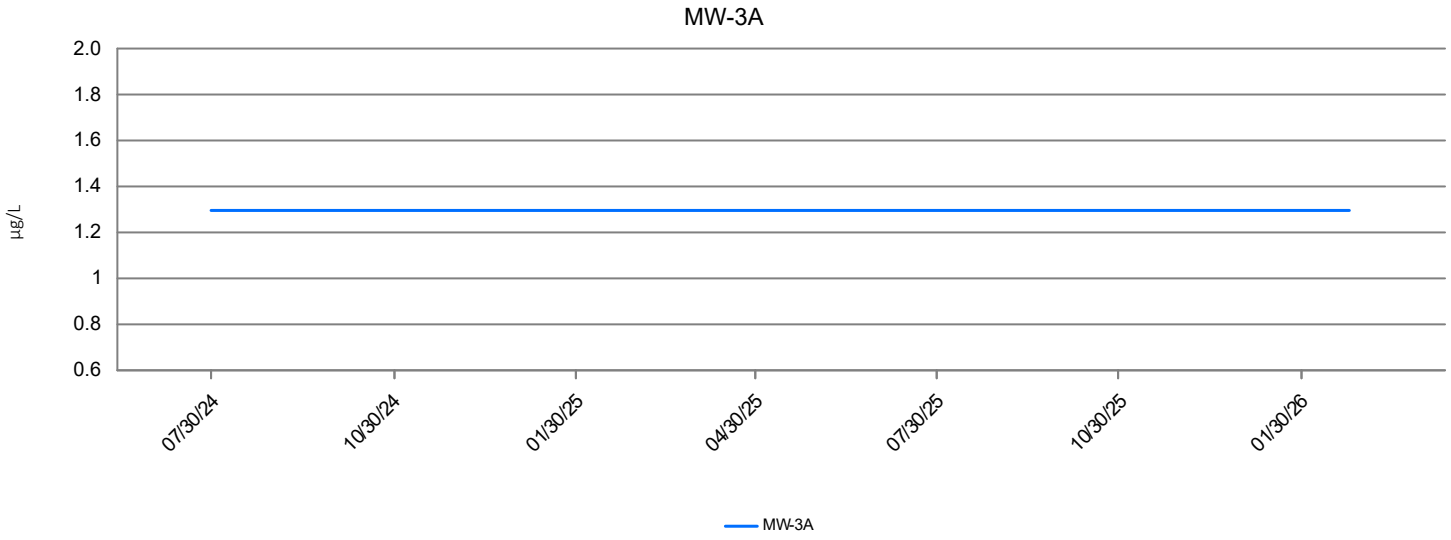
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Tin, Dissolved (µg/L)





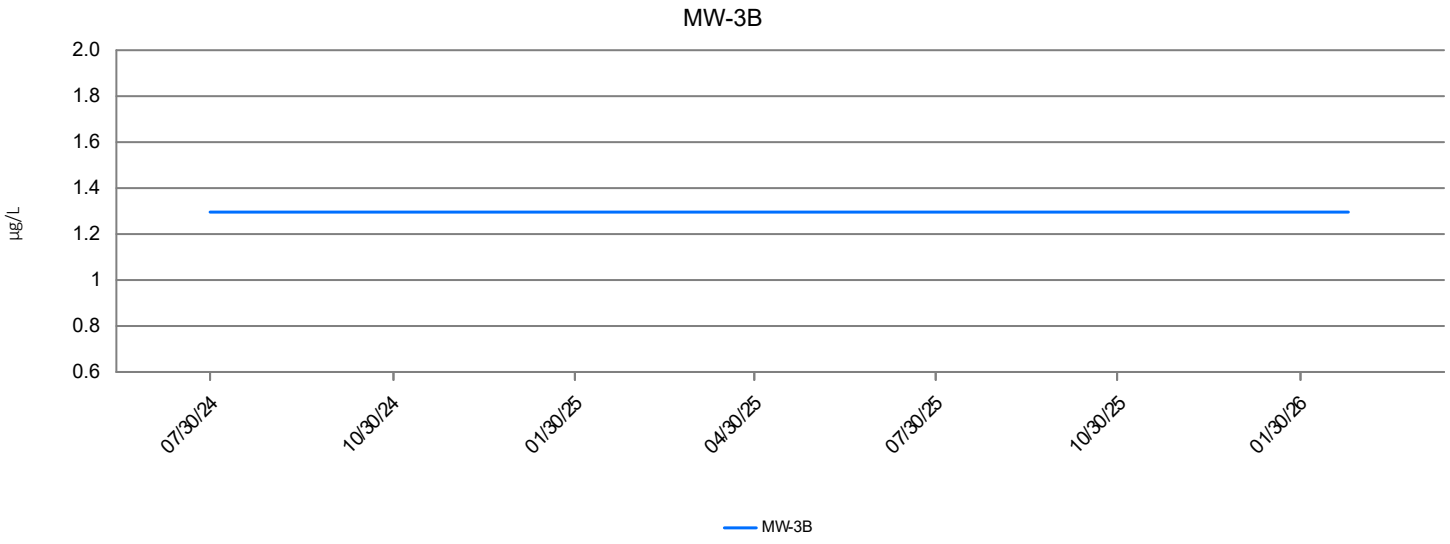


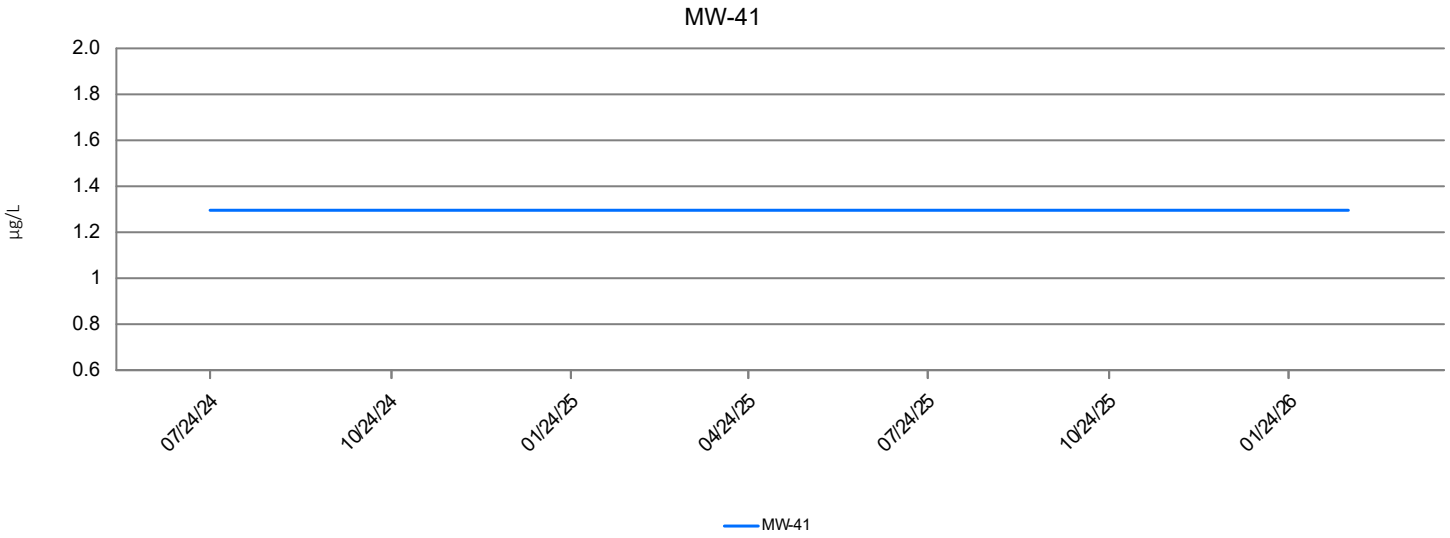
Variable Graphical Report

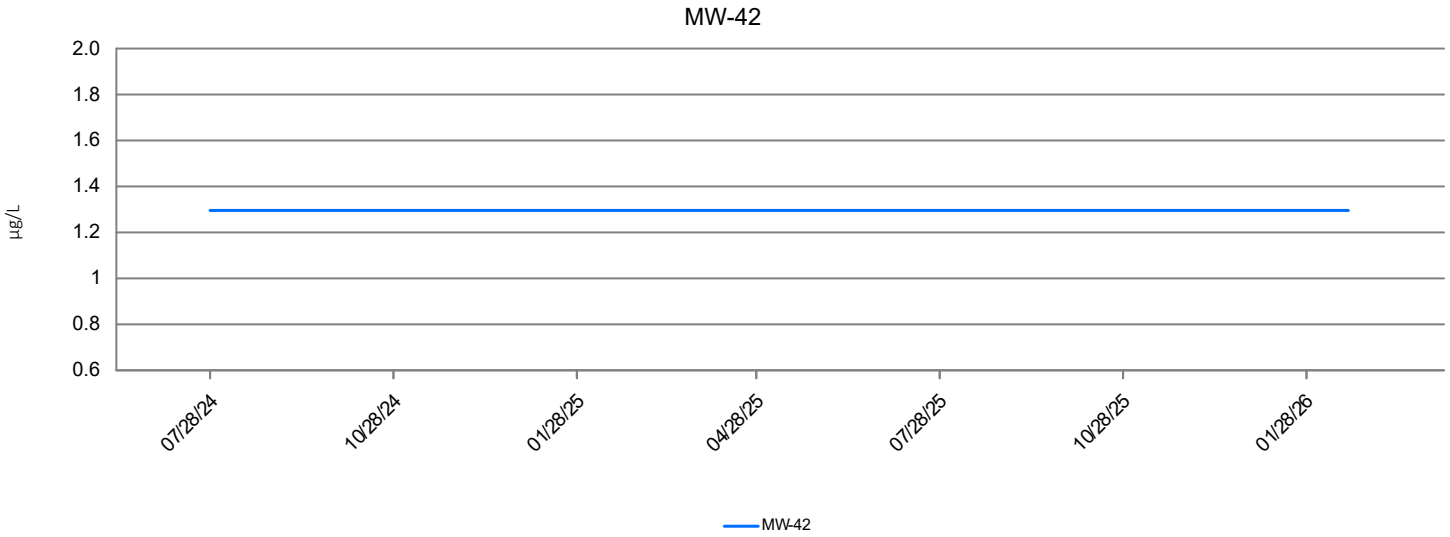
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Tin, Dissolved (µg/L)





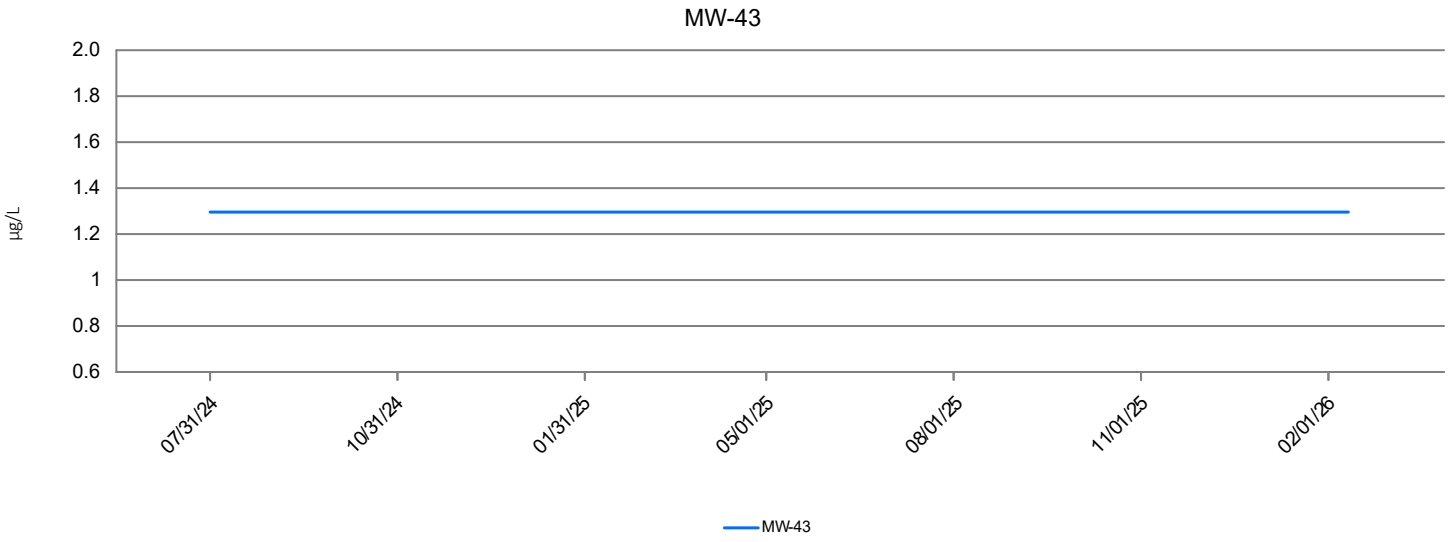


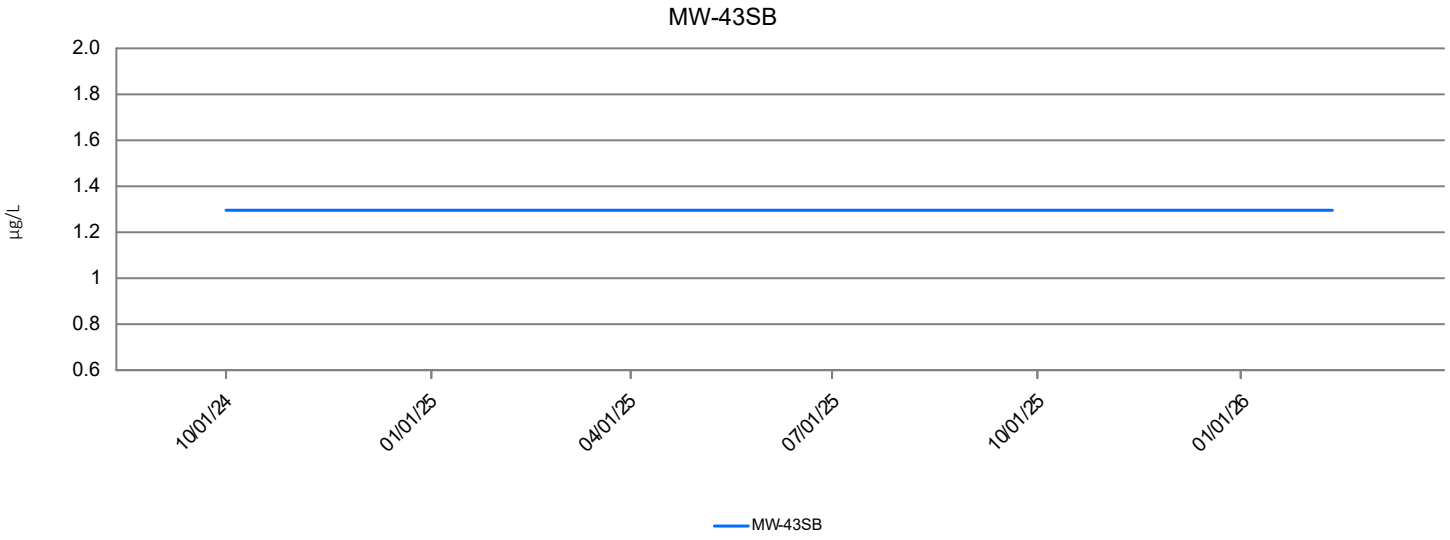
Variable Graphical Report

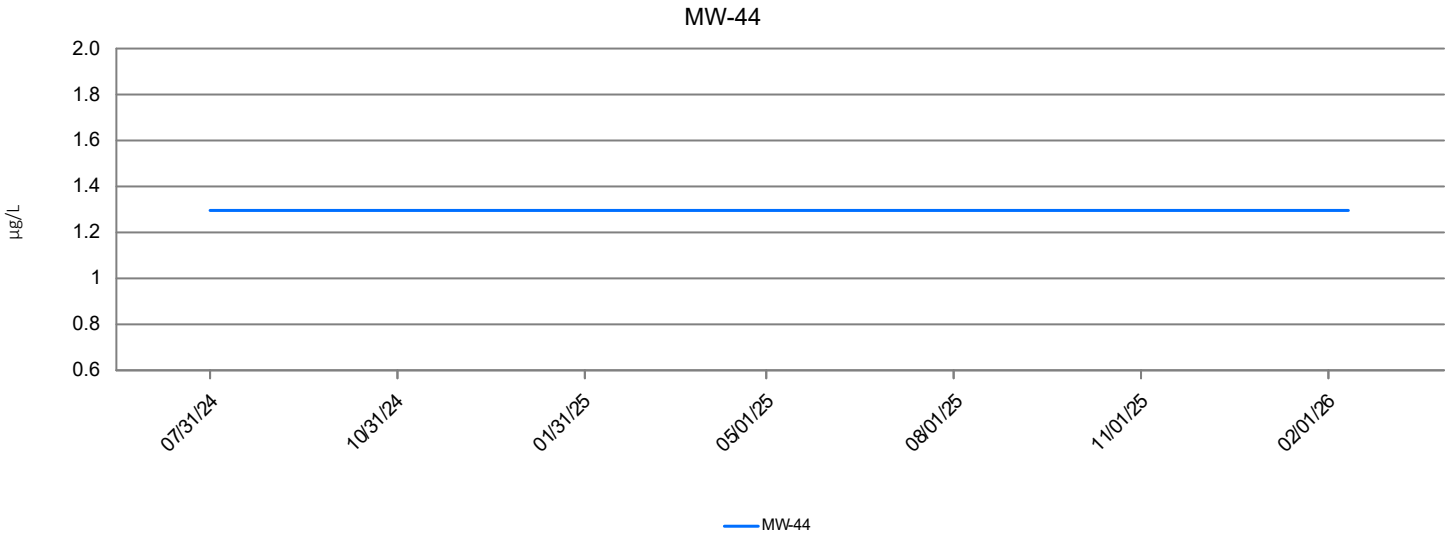
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Tin, Dissolved (µg/L)







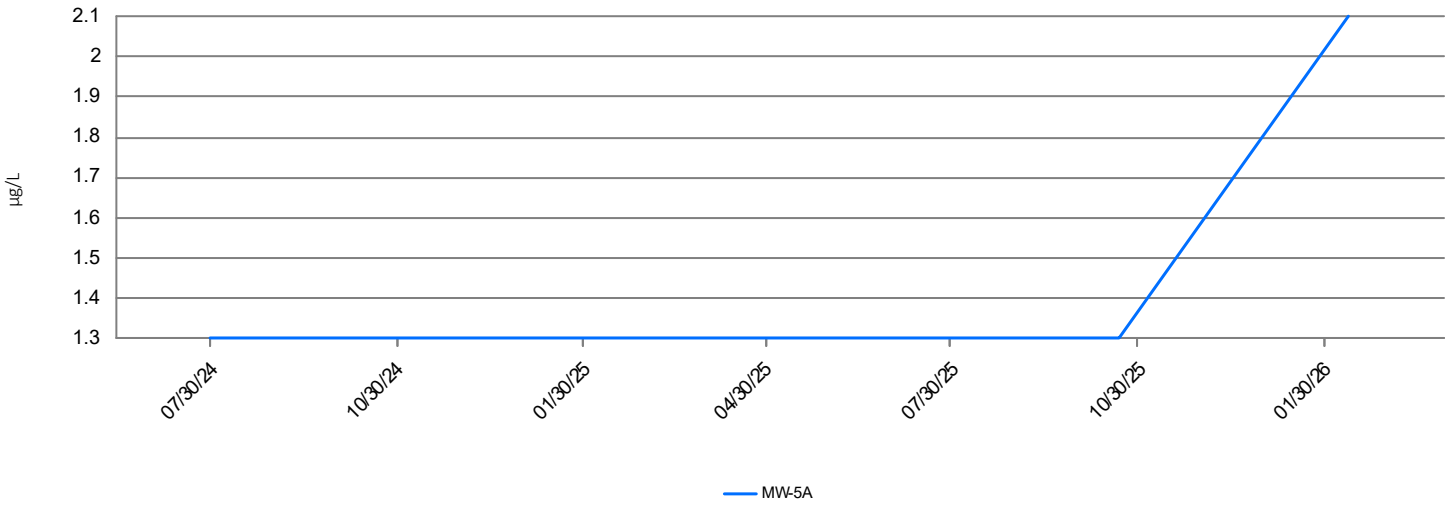
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

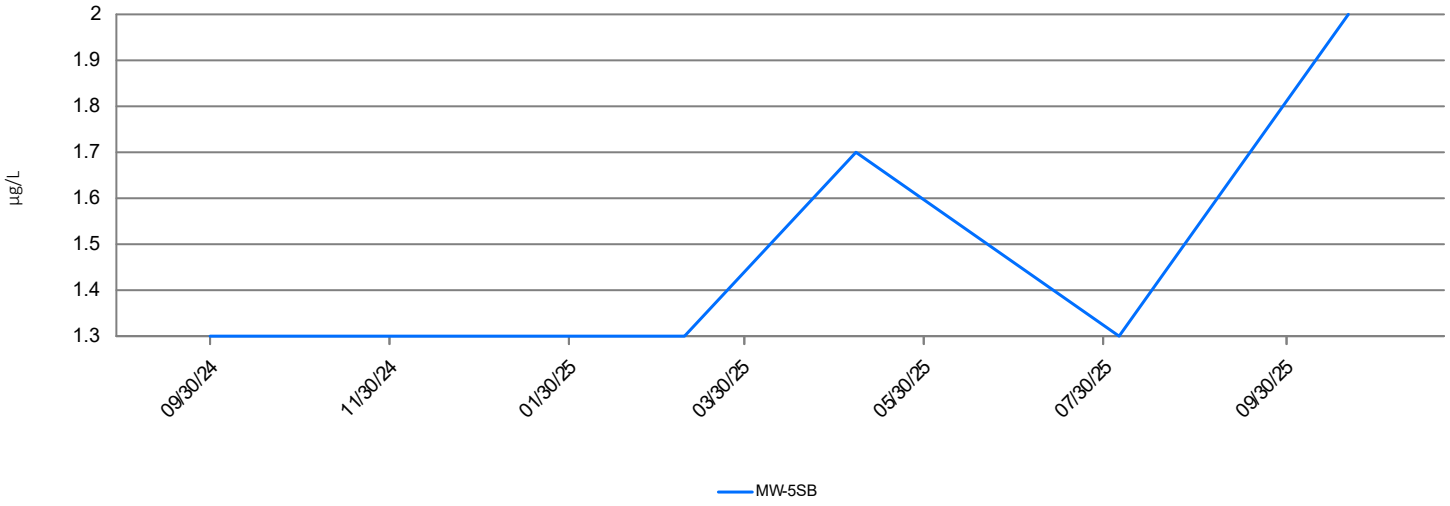
MonitorPro

No Group Selected, Tin, Dissolved (µg/L)

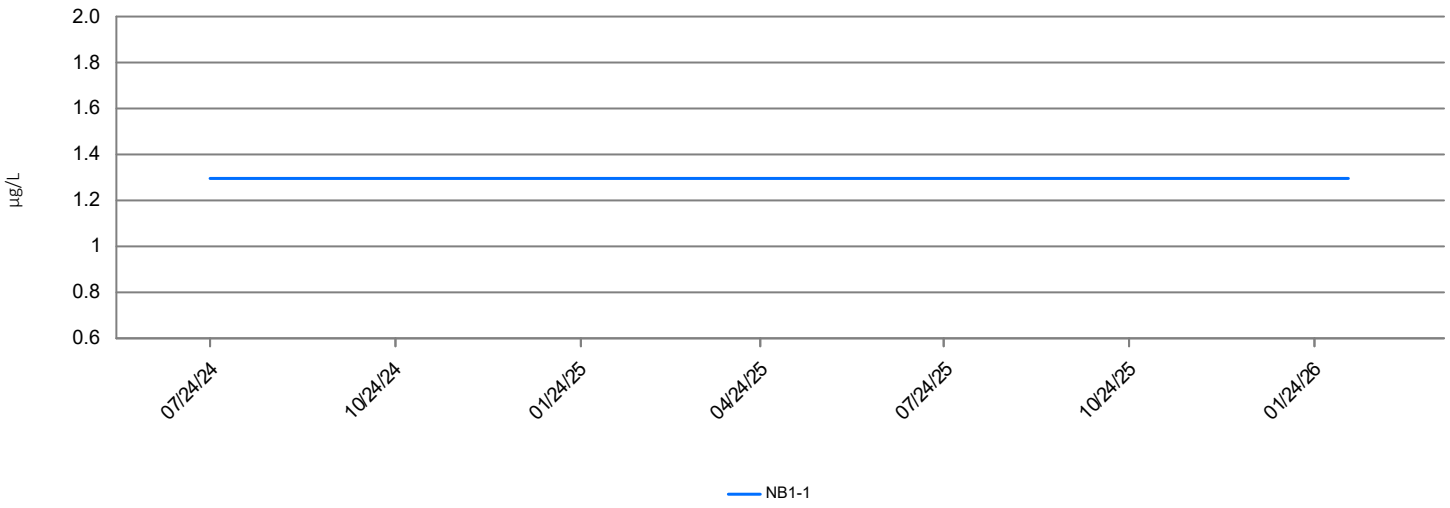
MW-5A



MW-5SB



NB1-1

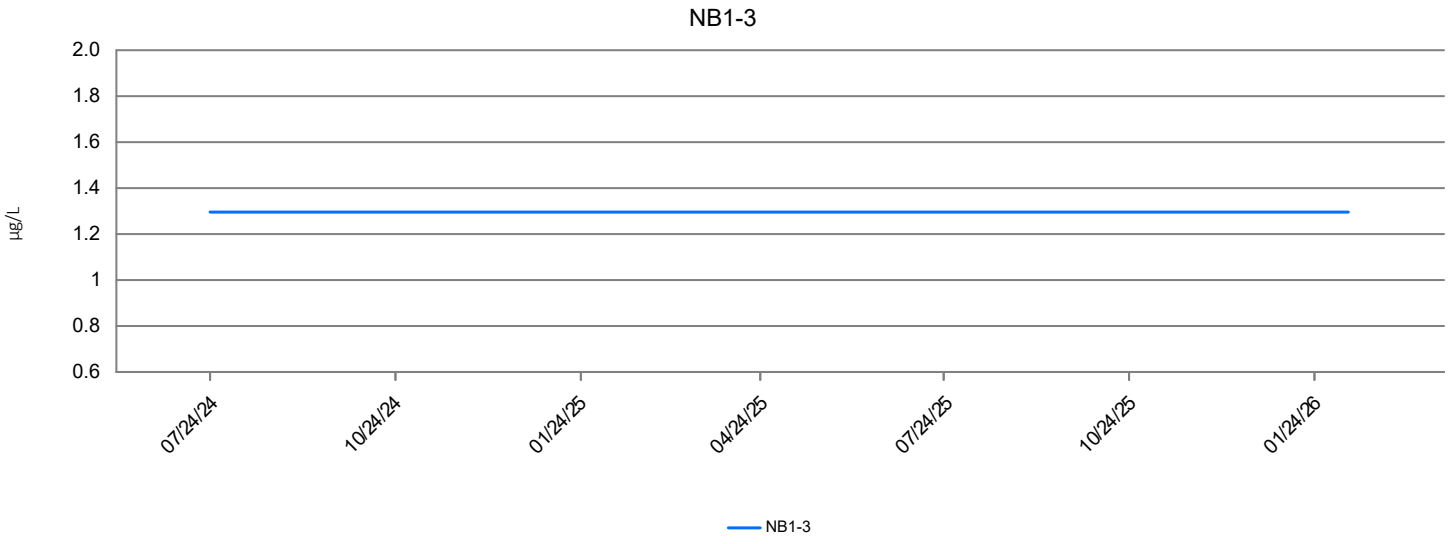


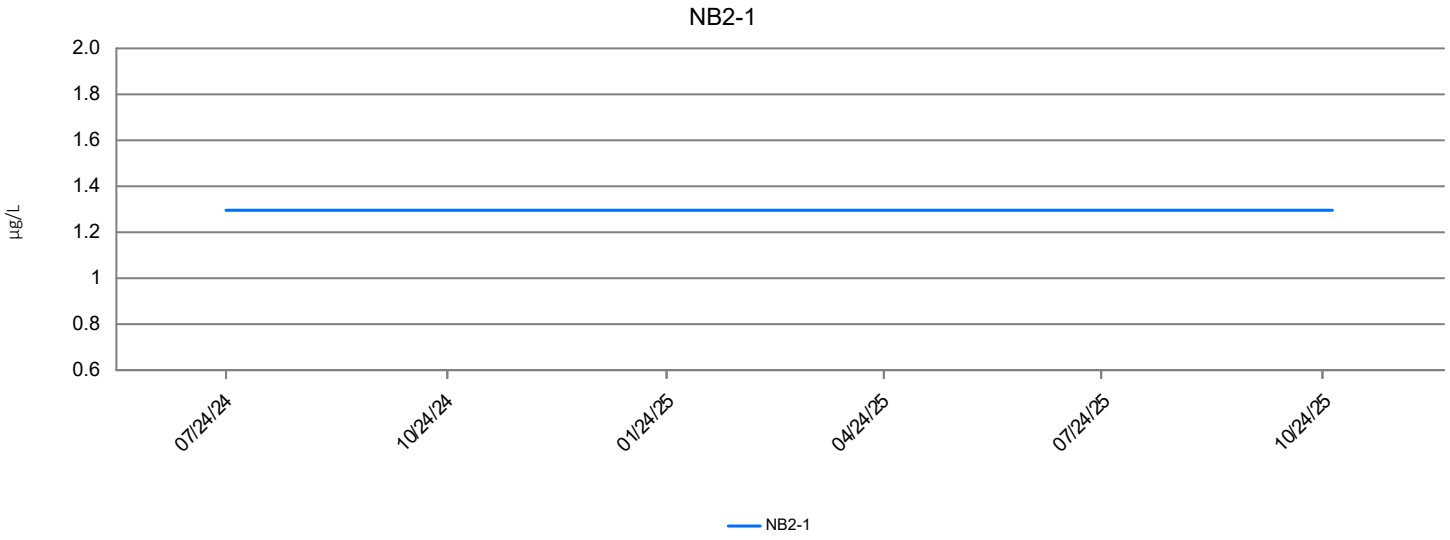
Variable Graphical Report

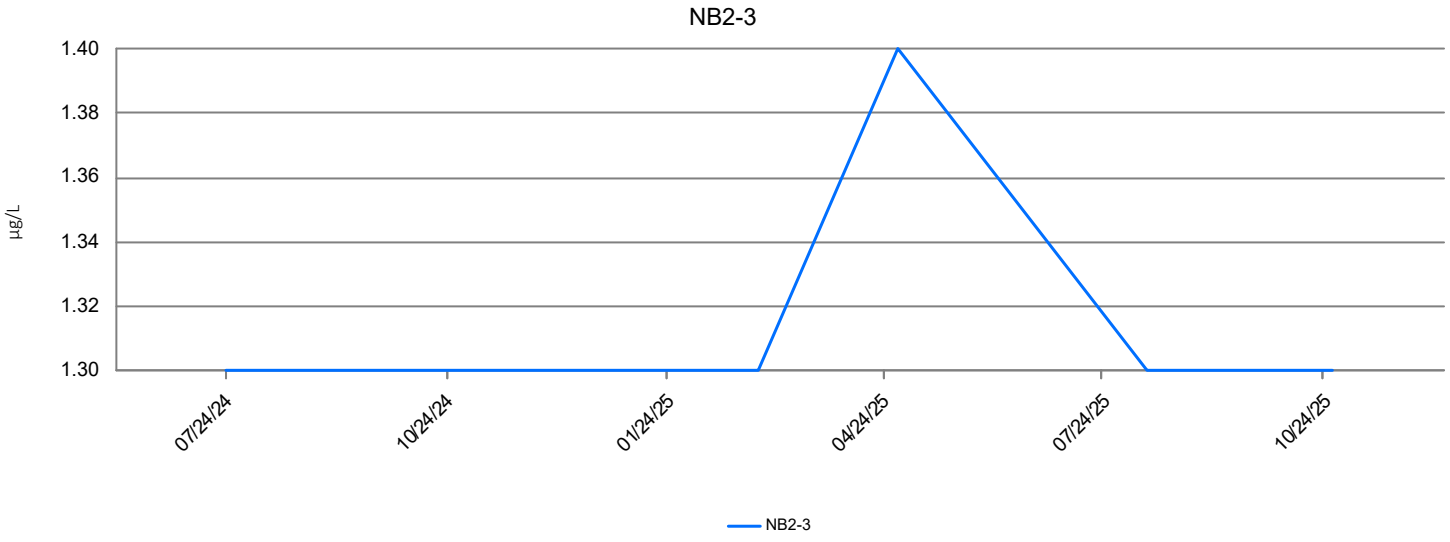
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Tin, Dissolved (µg/L)







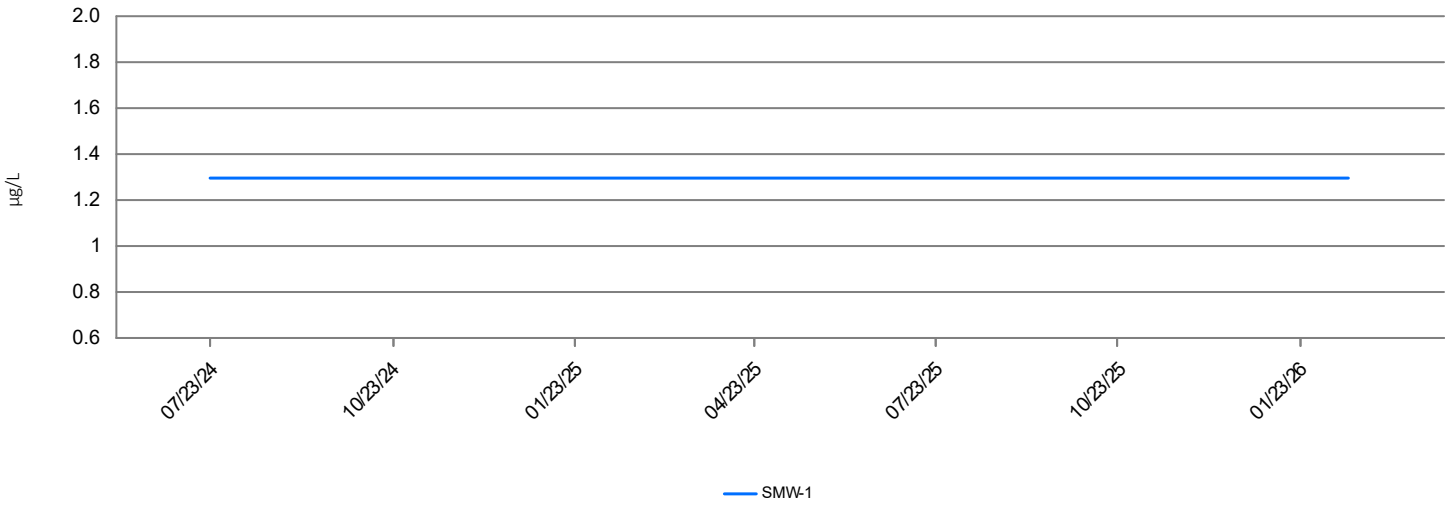
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

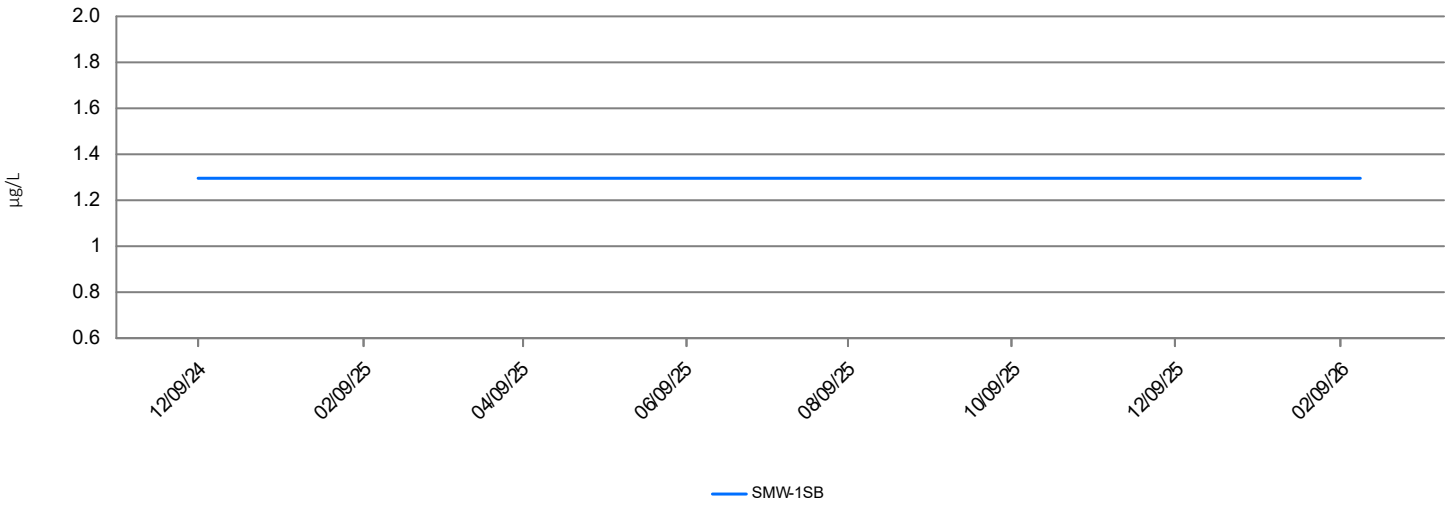
MonitorPro

No Group Selected, Tin, Dissolved (µg/L)

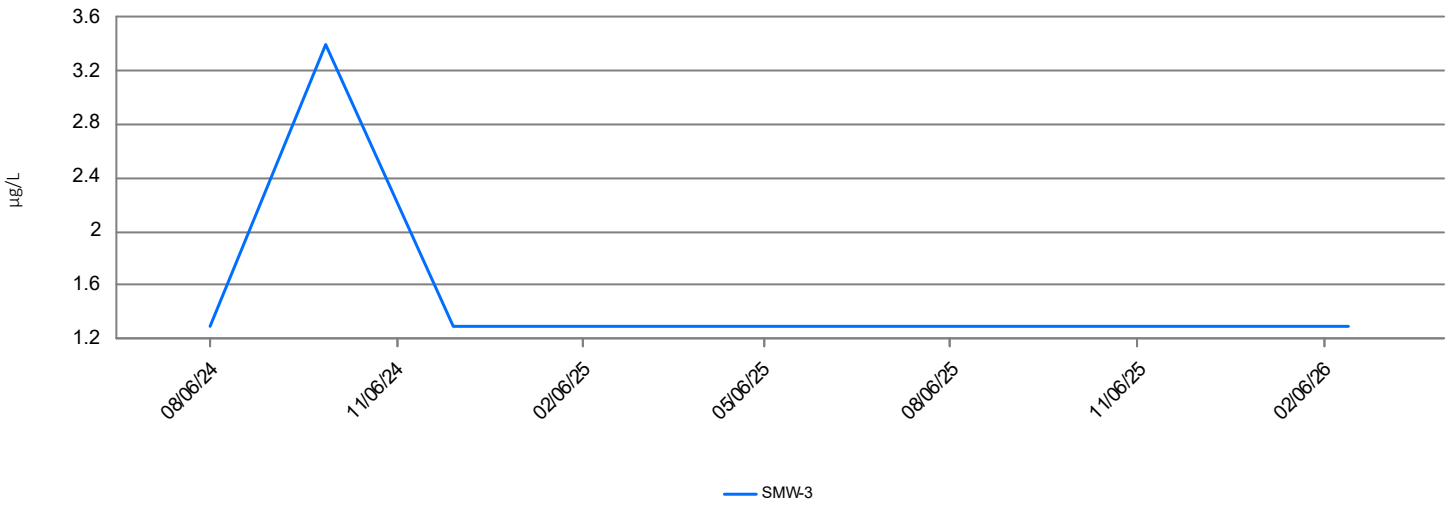
SMW-1



SMW-1SB



SMW-3

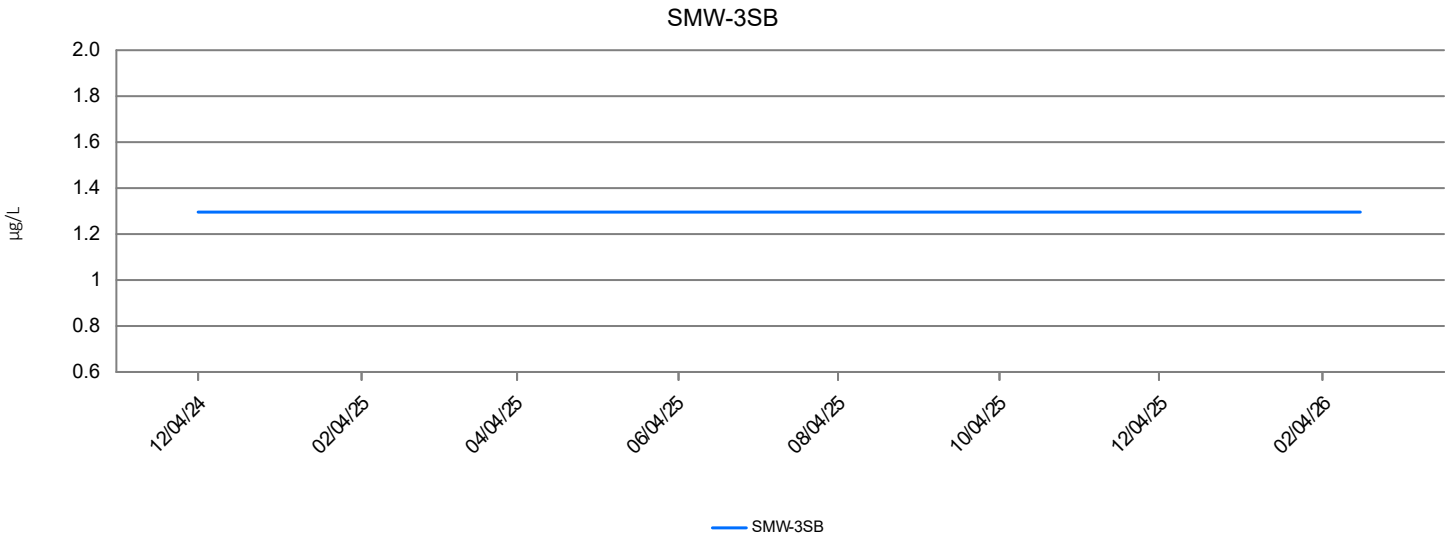


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Tin, Dissolved (µg/L)

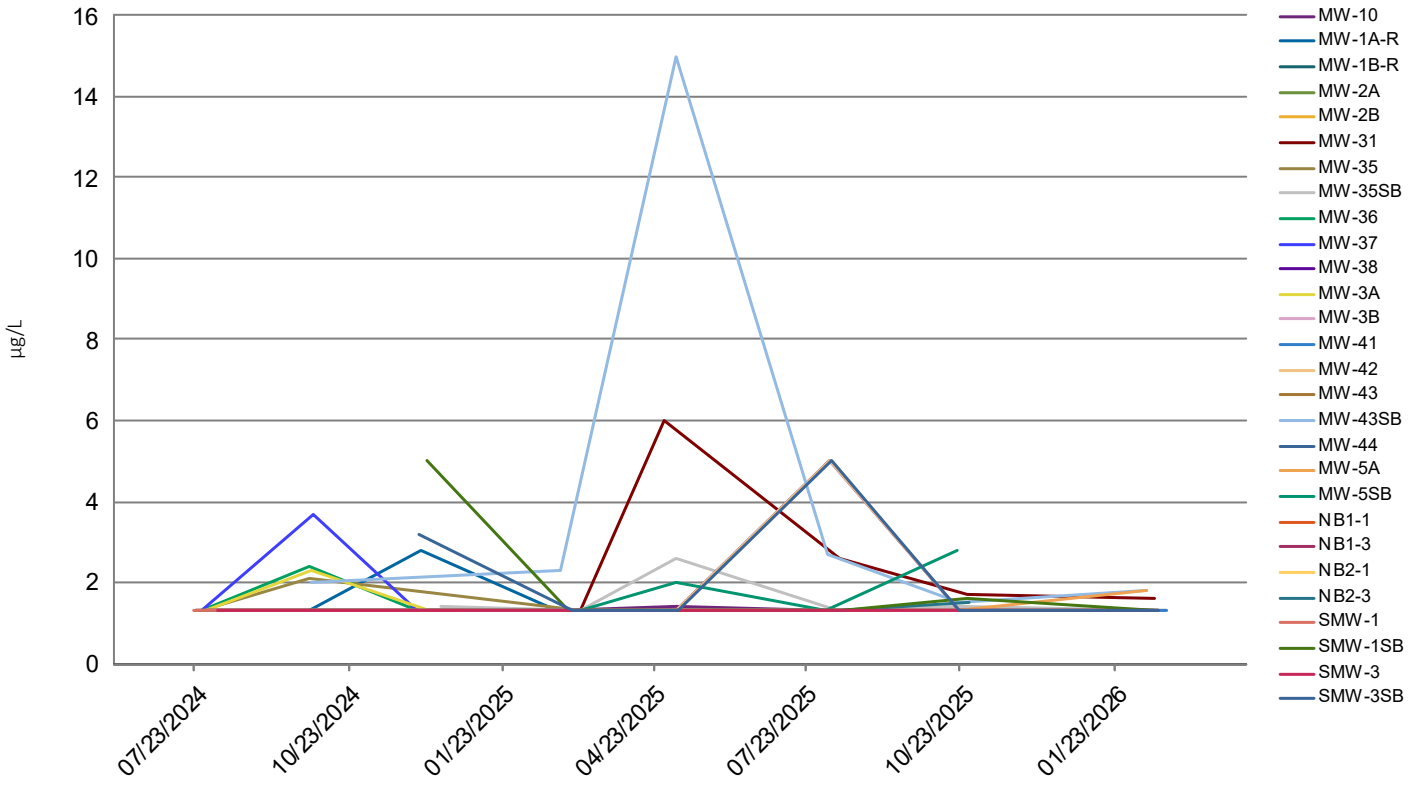


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Tin, Total Recoverable (µg/L)

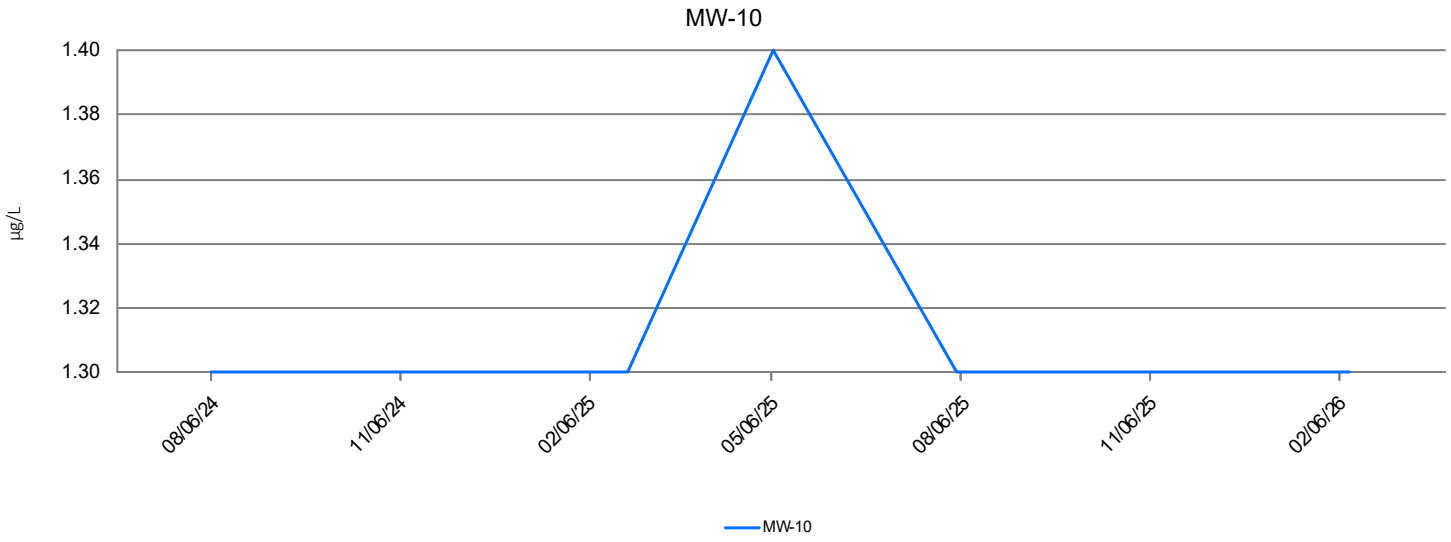


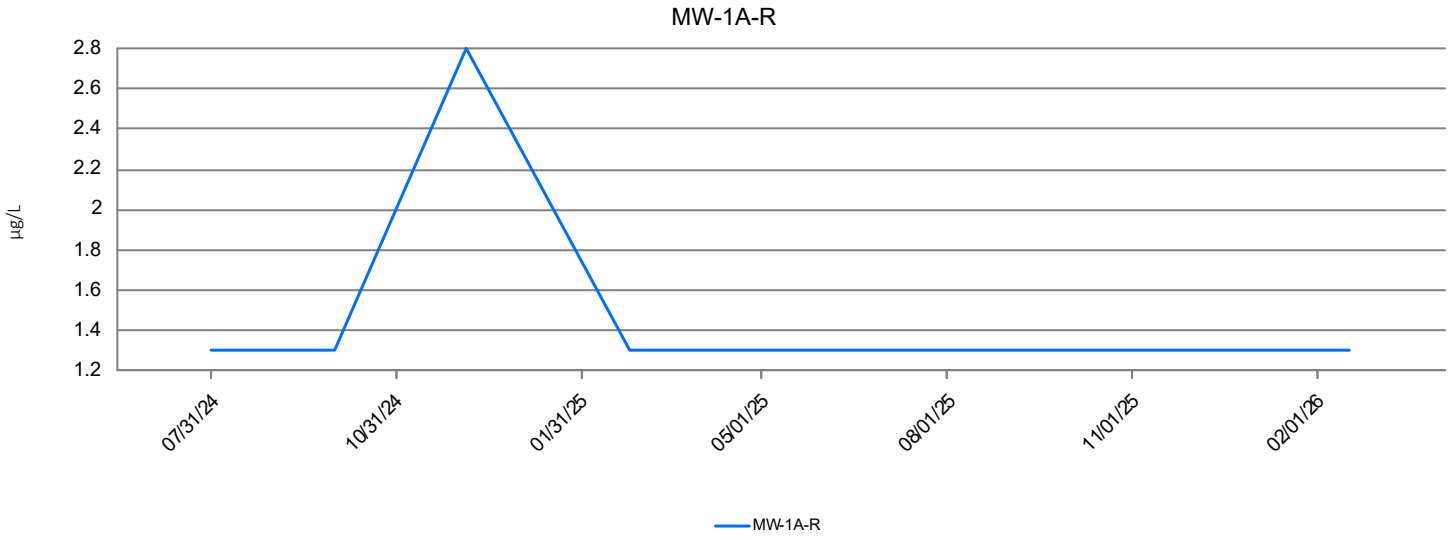
Variable Graphical Report

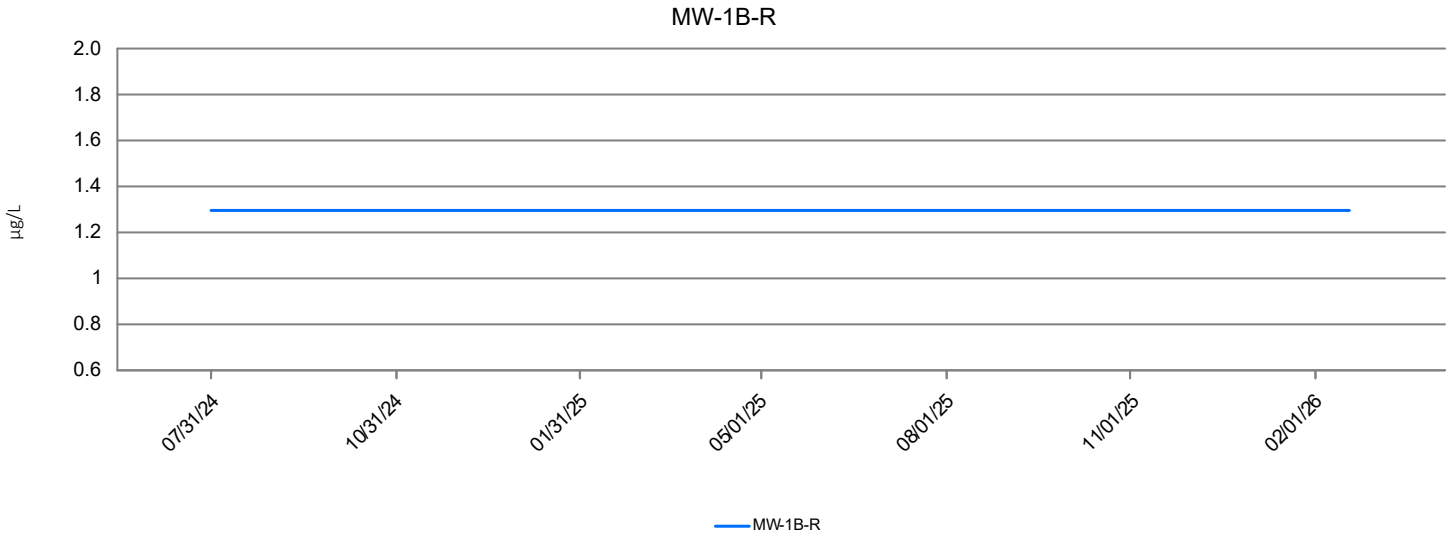
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Tin, Total Recoverable (µg/L)







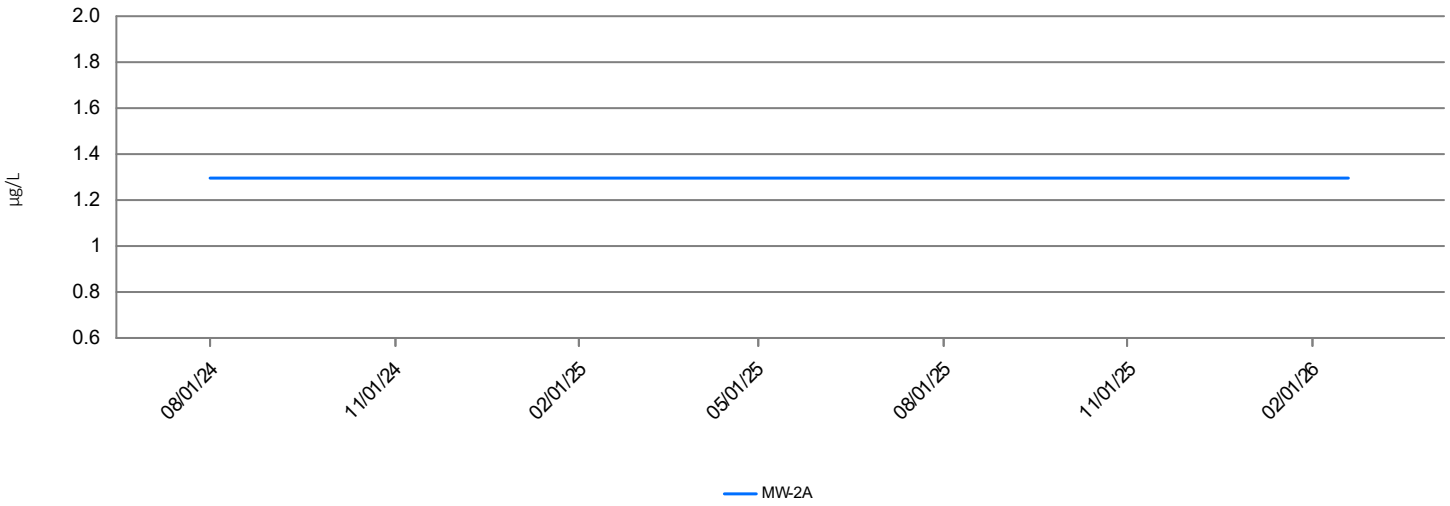
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

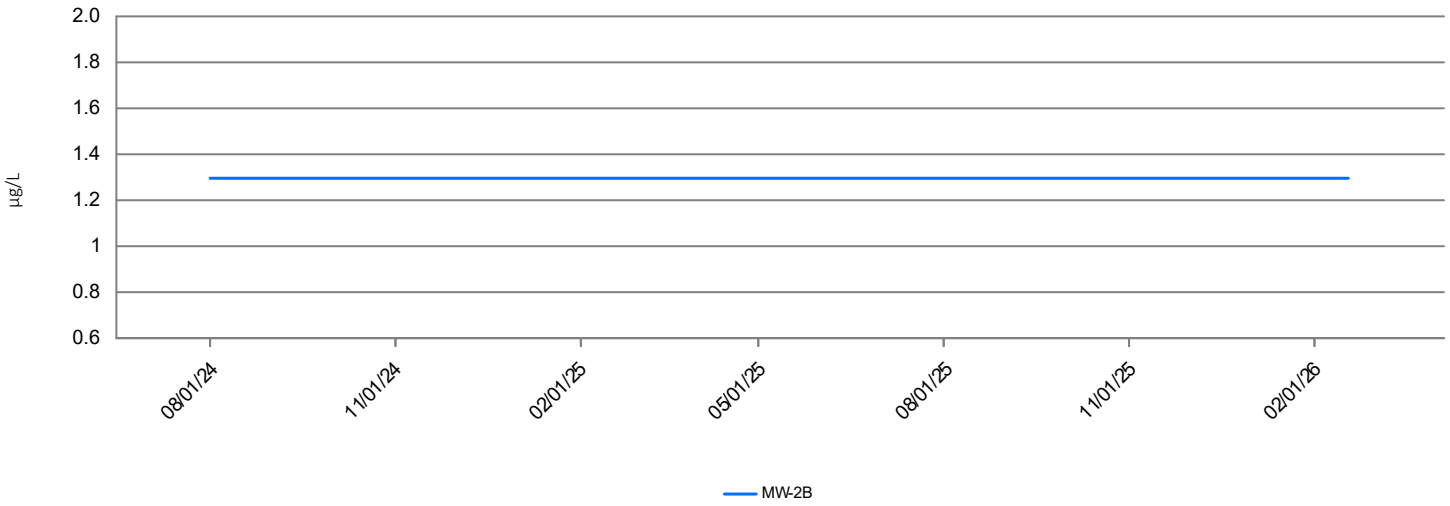
MonitorPro

No Group Selected, Tin, Total Recoverable (µg/L)

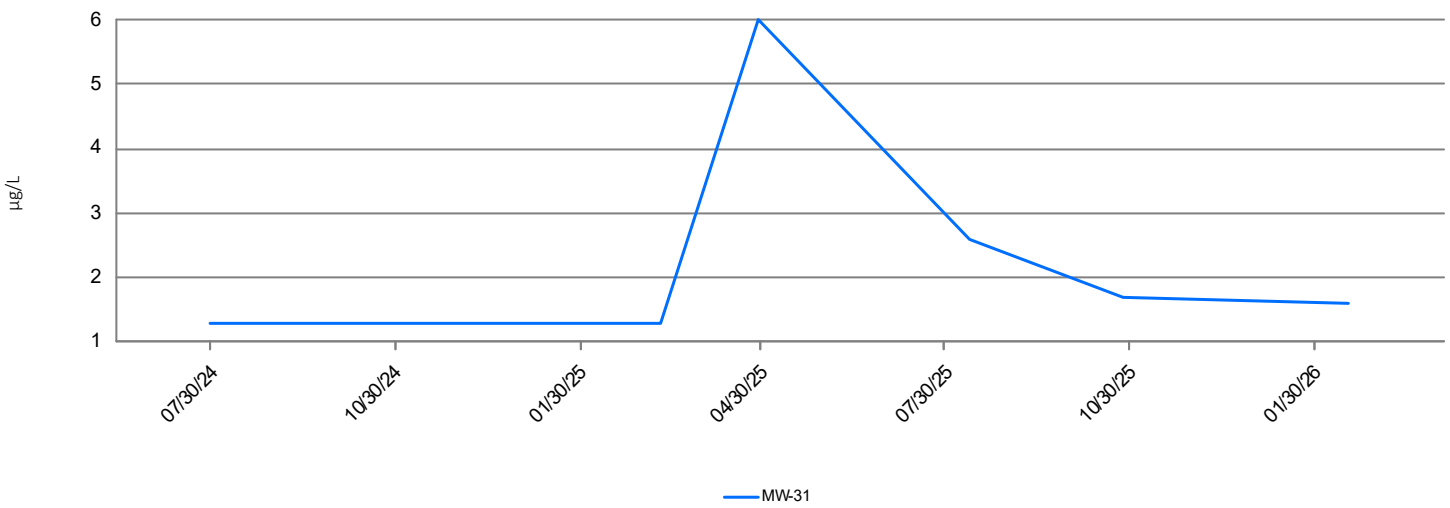
MW-2A



MW-2B



MW-31

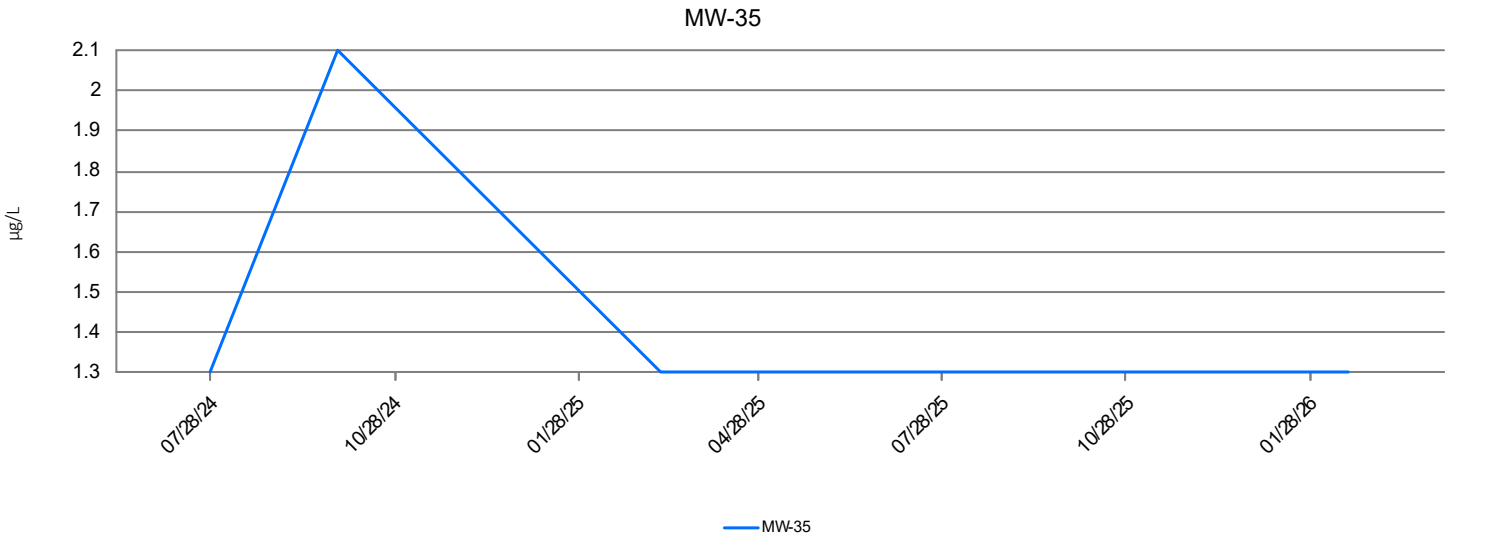


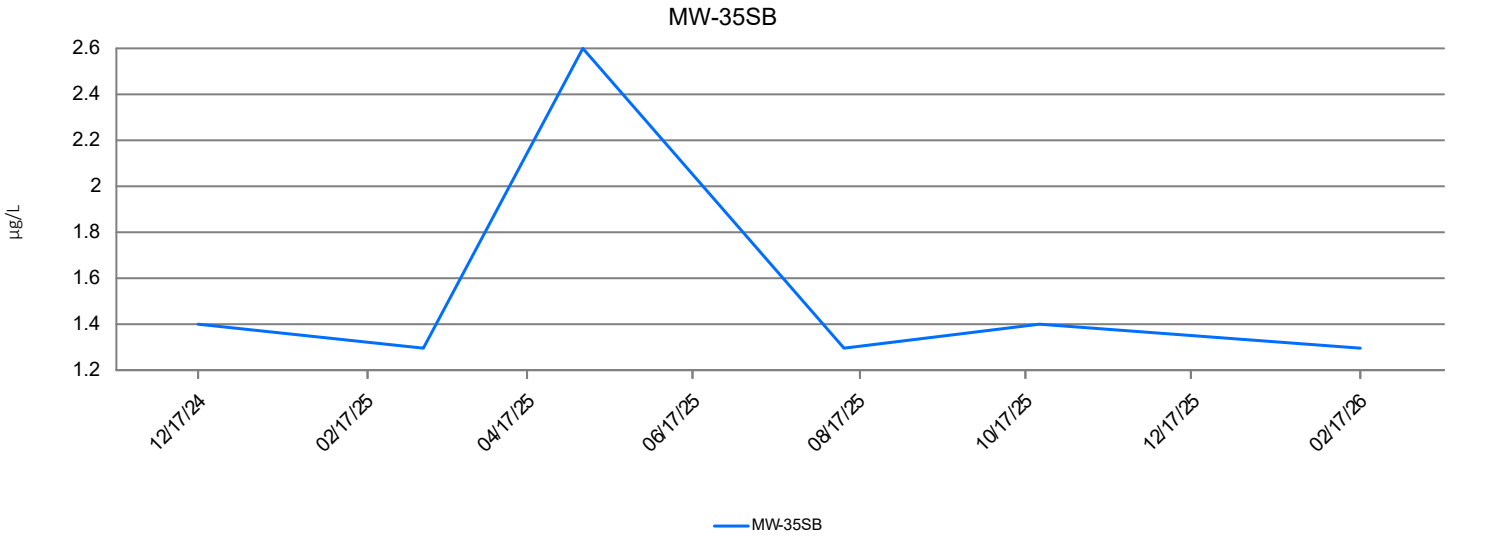
Variable Graphical Report

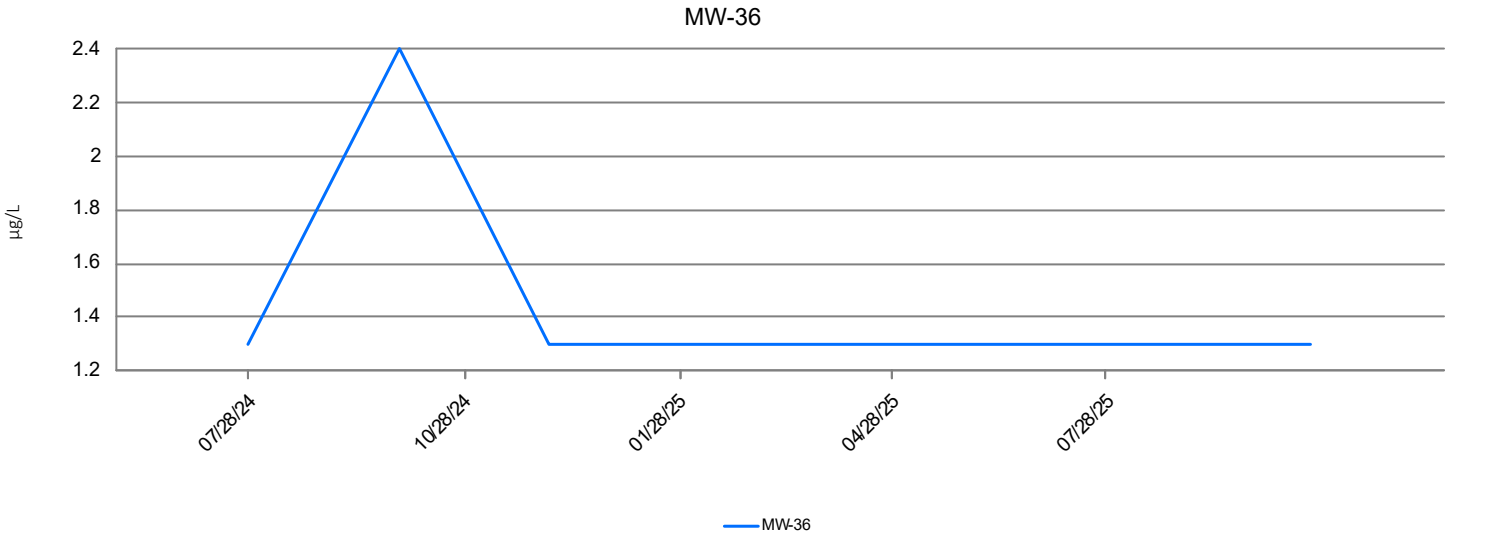
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Tin, Total Recoverable (µg/L)







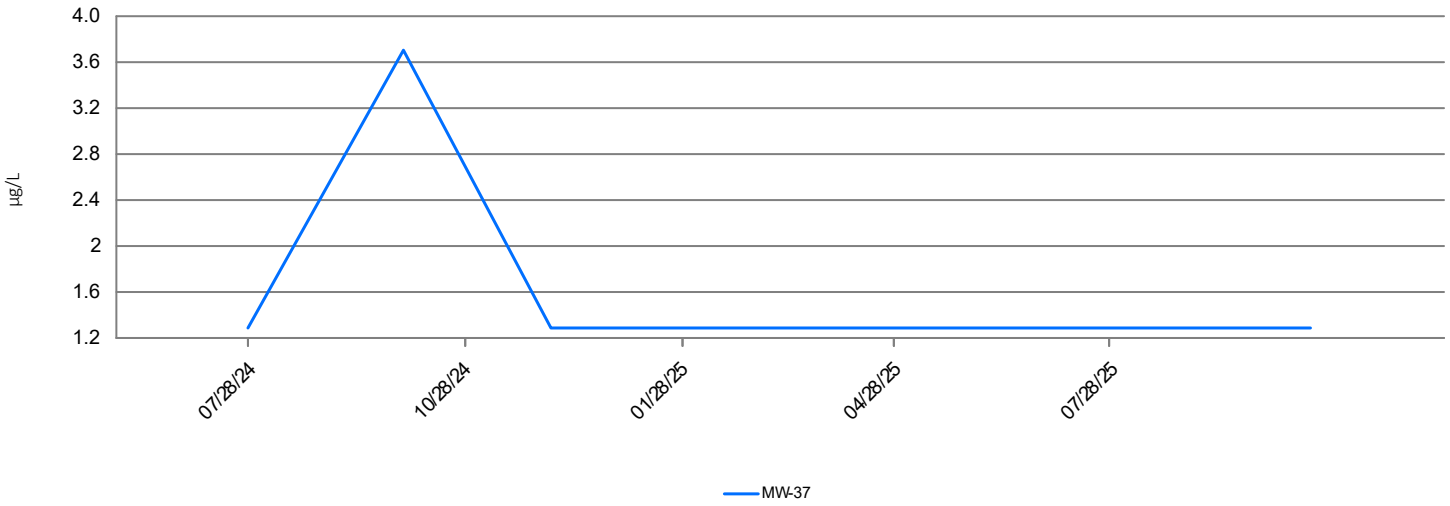
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

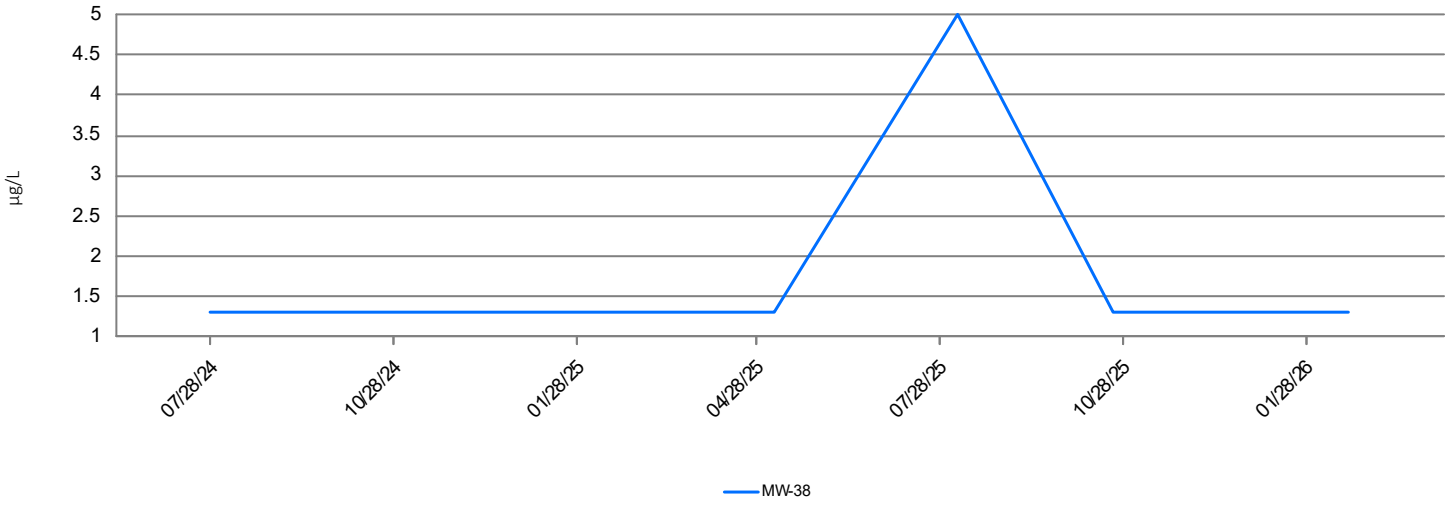
MonitorPro

No Group Selected, Tin, Total Recoverable (µg/L)

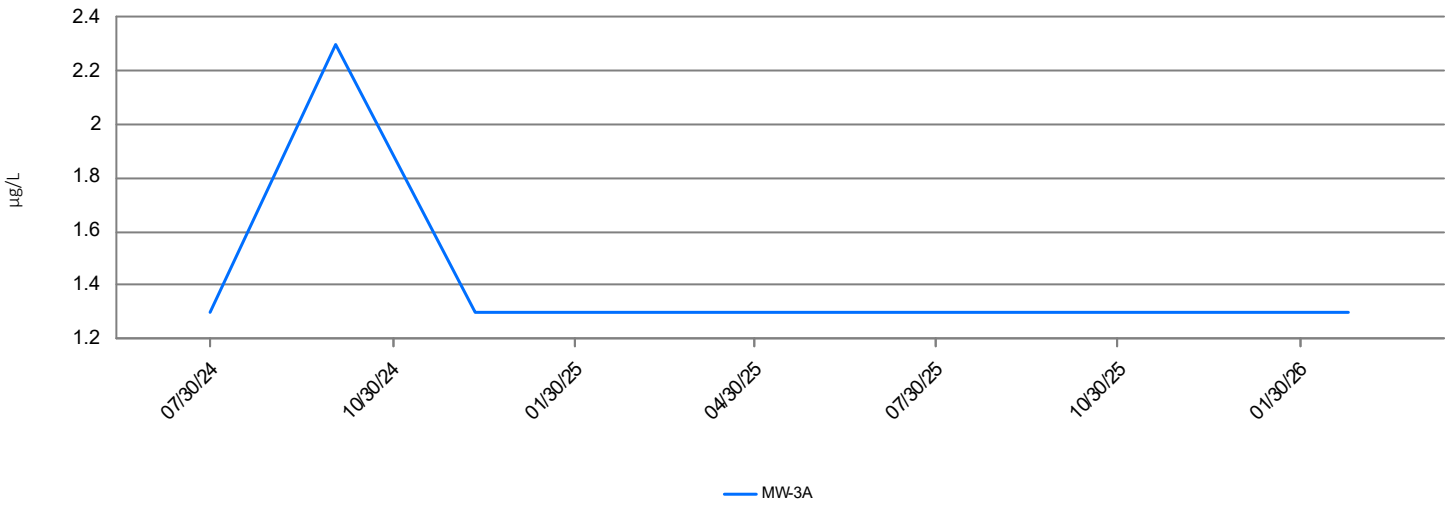
MW-37



MW-38



MW-3A

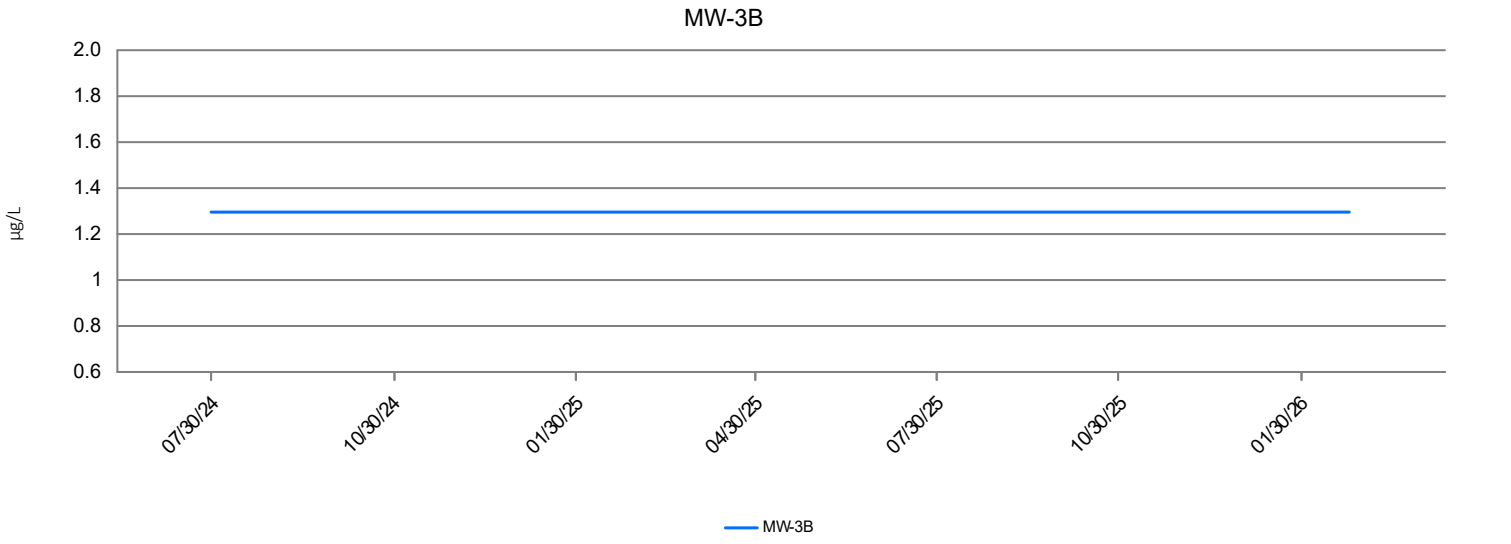


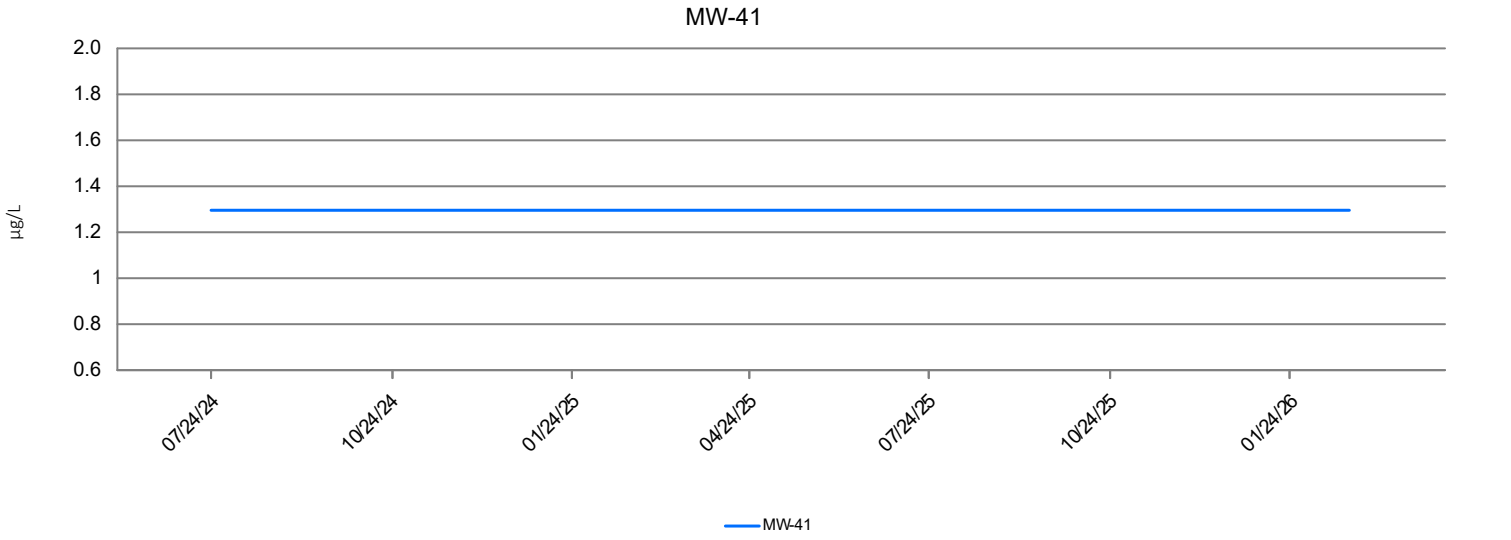
Variable Graphical Report

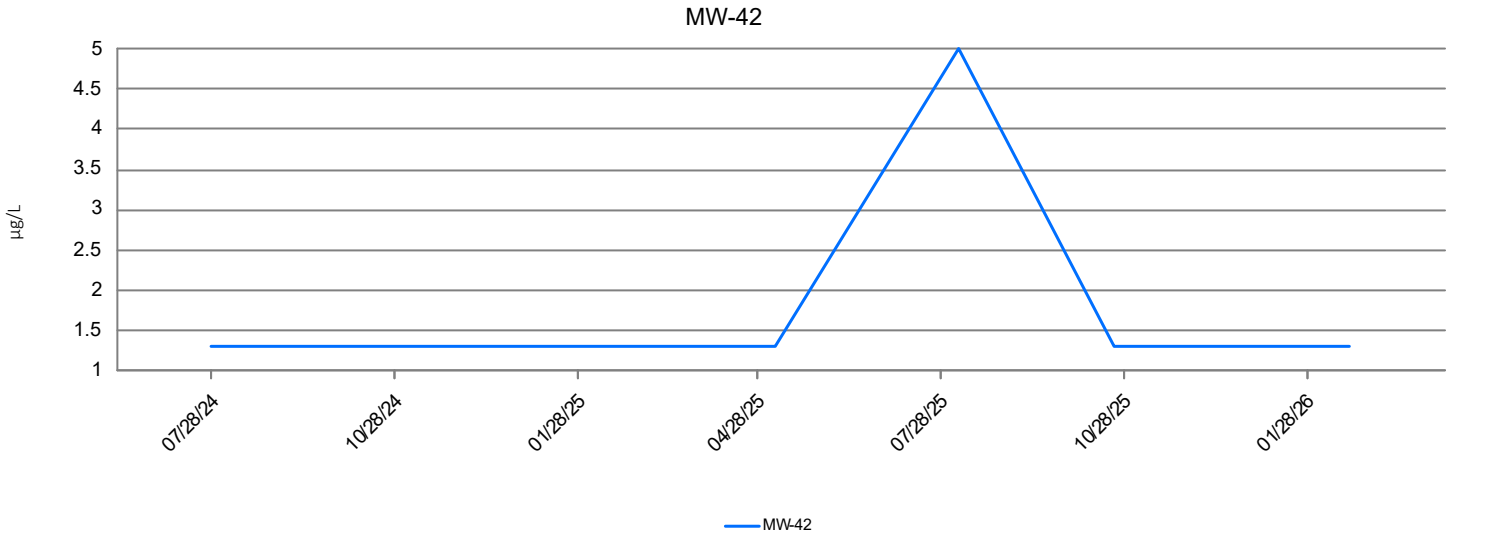
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Tin, Total Recoverable (µg/L)







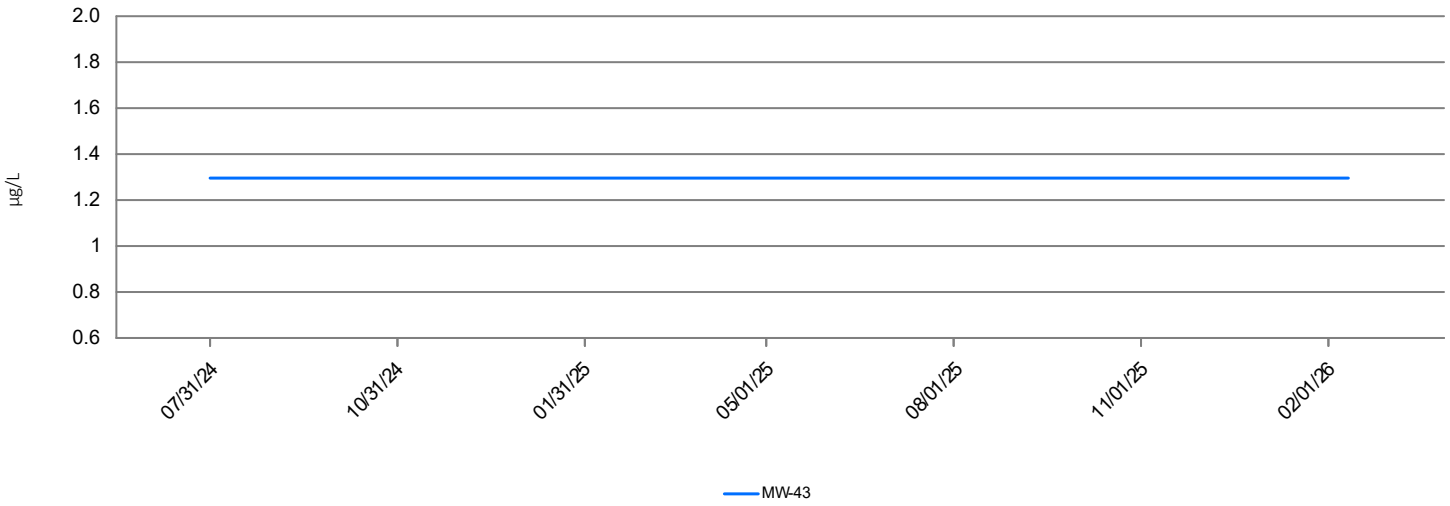
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

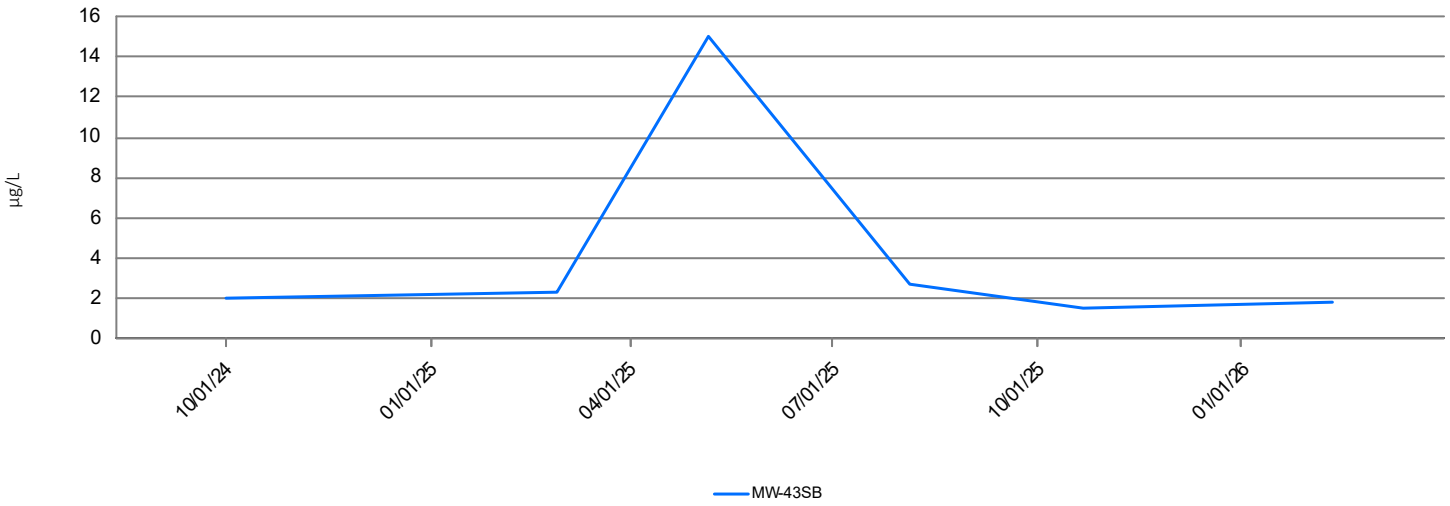
MonitorPro

No Group Selected, Tin, Total Recoverable (µg/L)

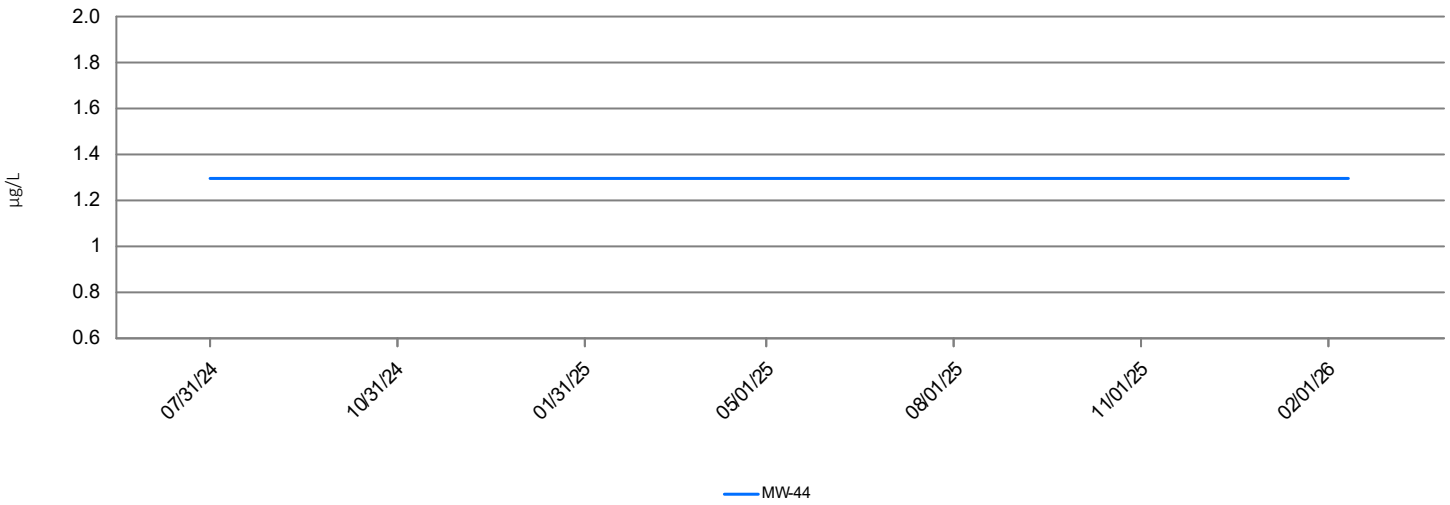
MW-43



MW-43SB



MW-44



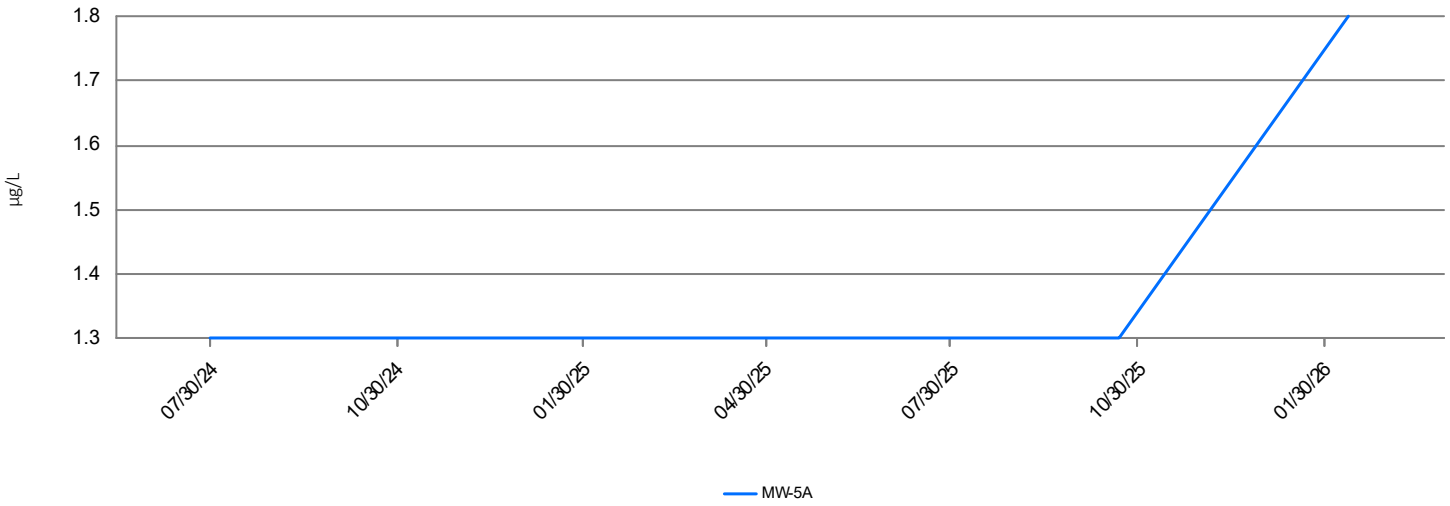
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

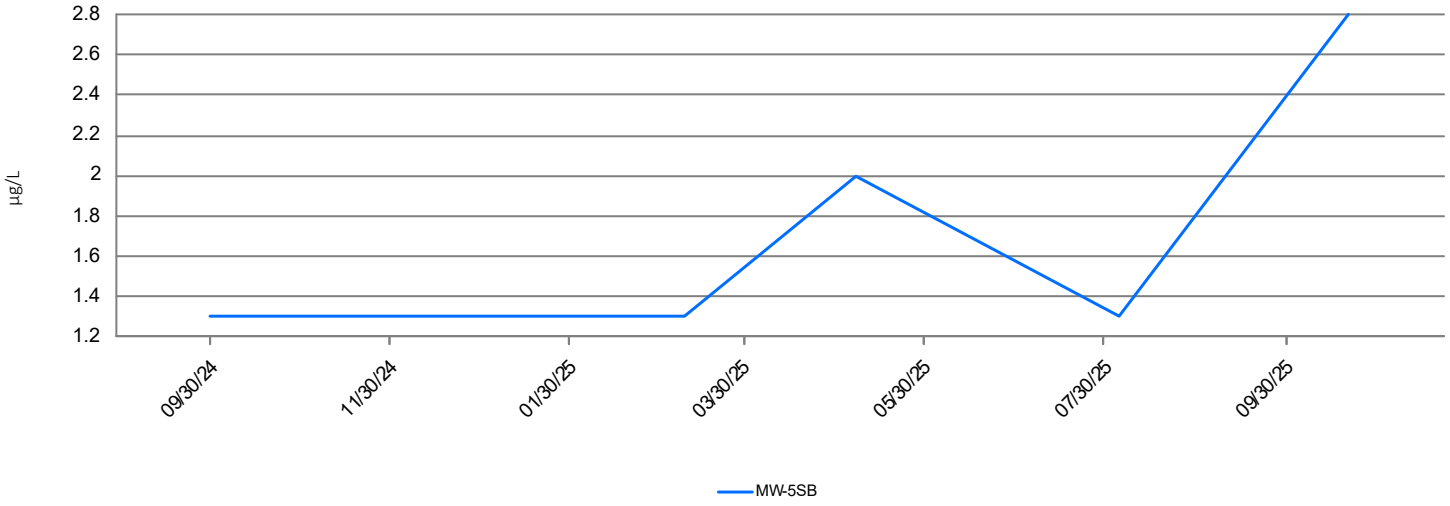
MonitorPro

No Group Selected, Tin, Total Recoverable (µg/L)

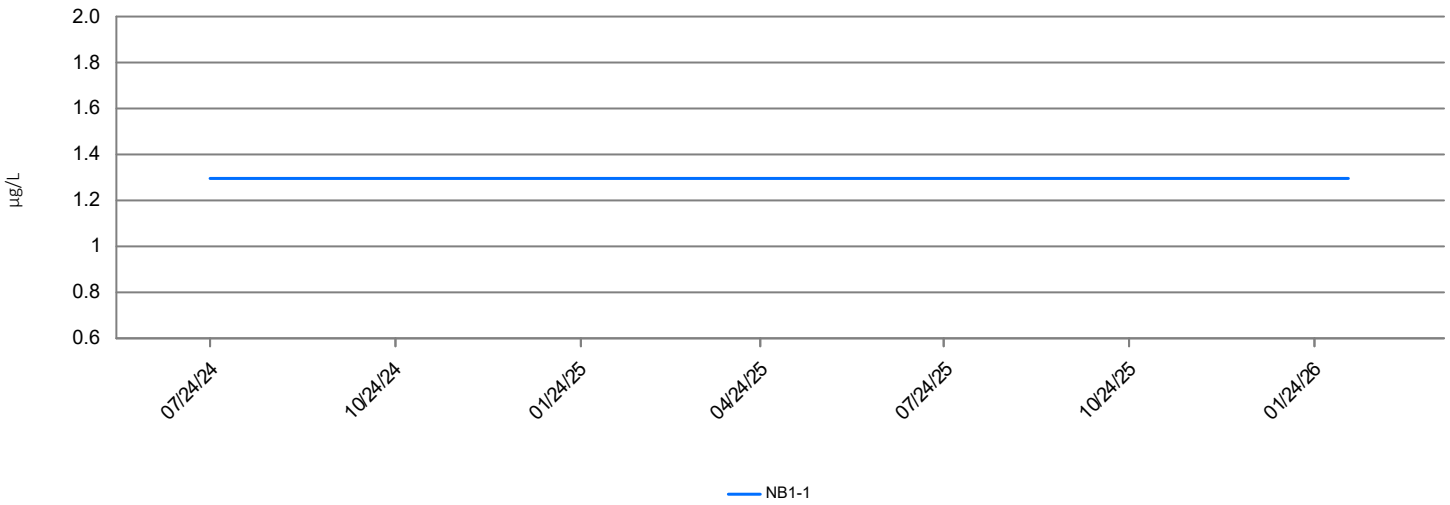
MW-5A



MW-5SB



NB1-1



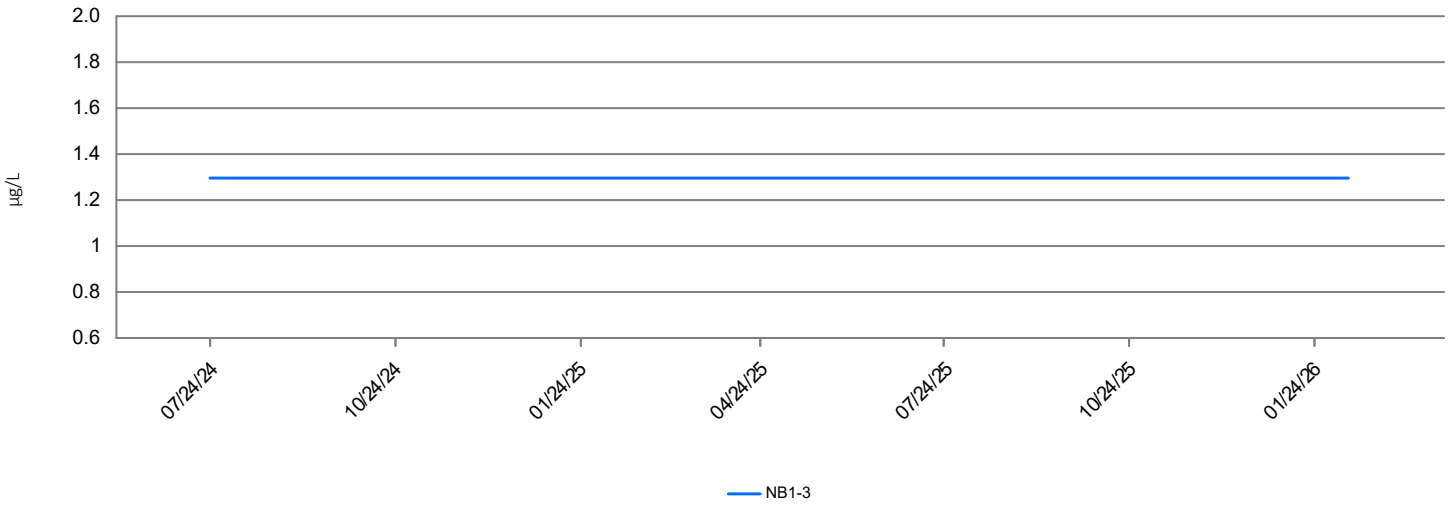
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

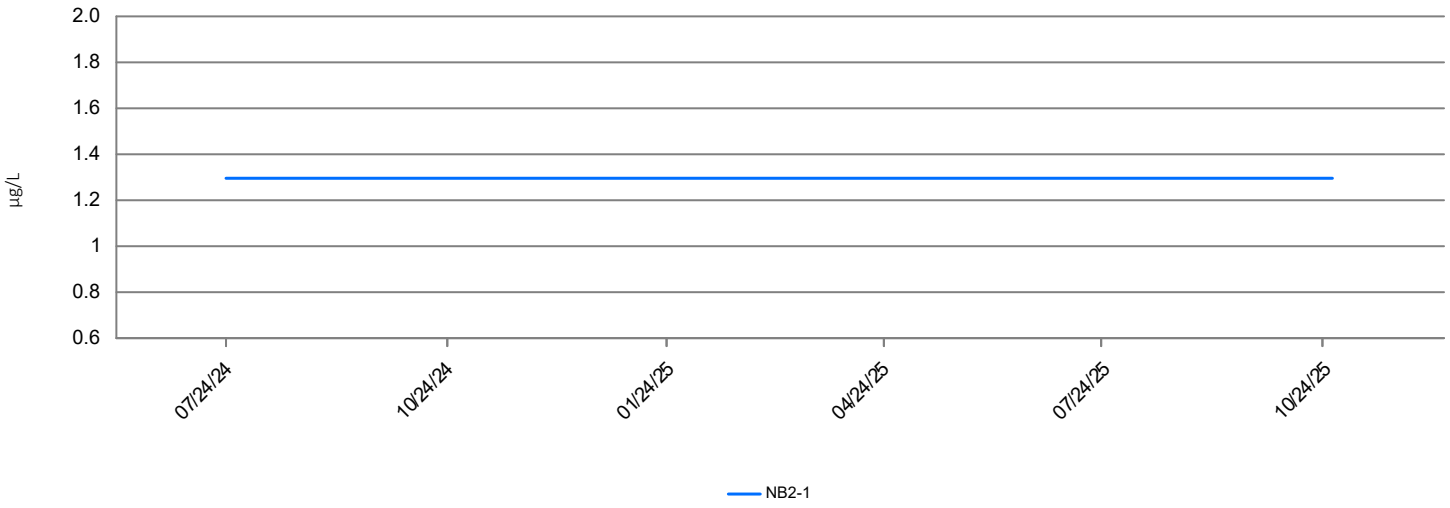
MonitorPro

No Group Selected, Tin, Total Recoverable (µg/L)

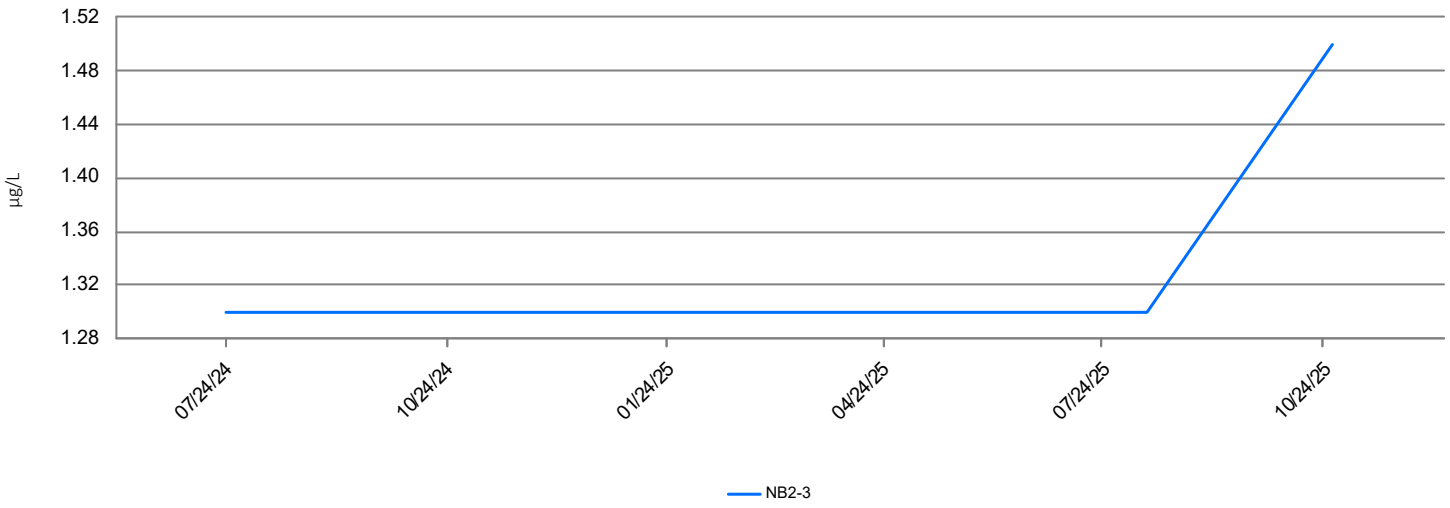
NB1-3



NB2-1



NB2-3

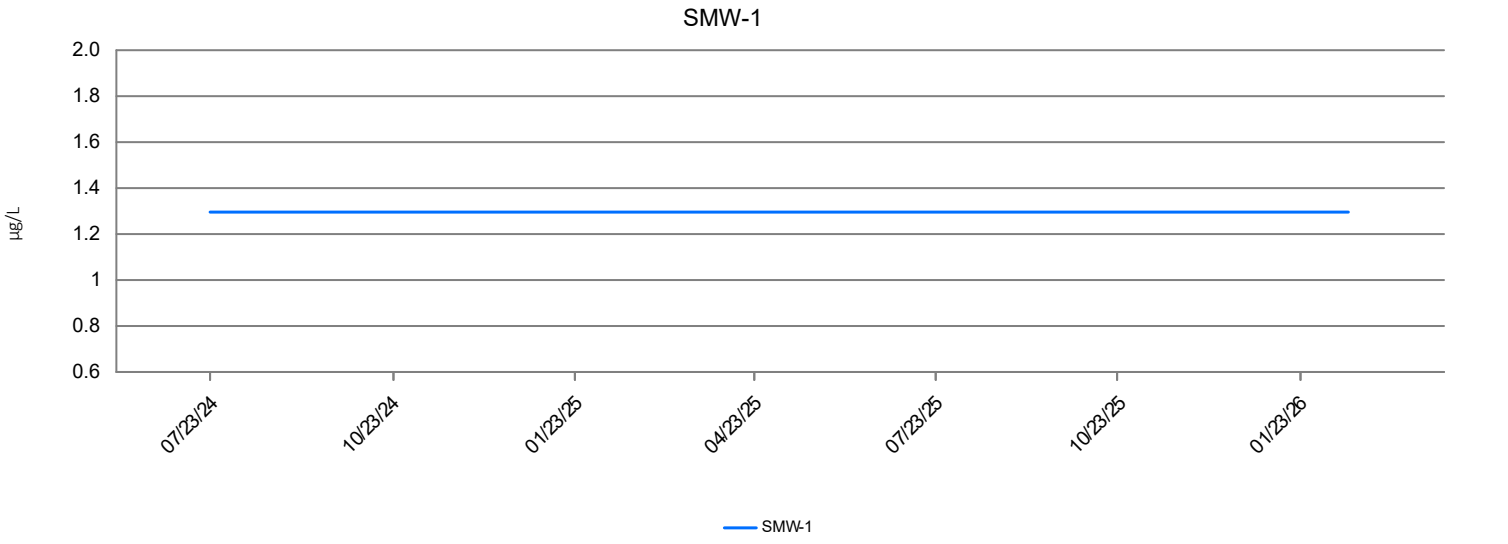


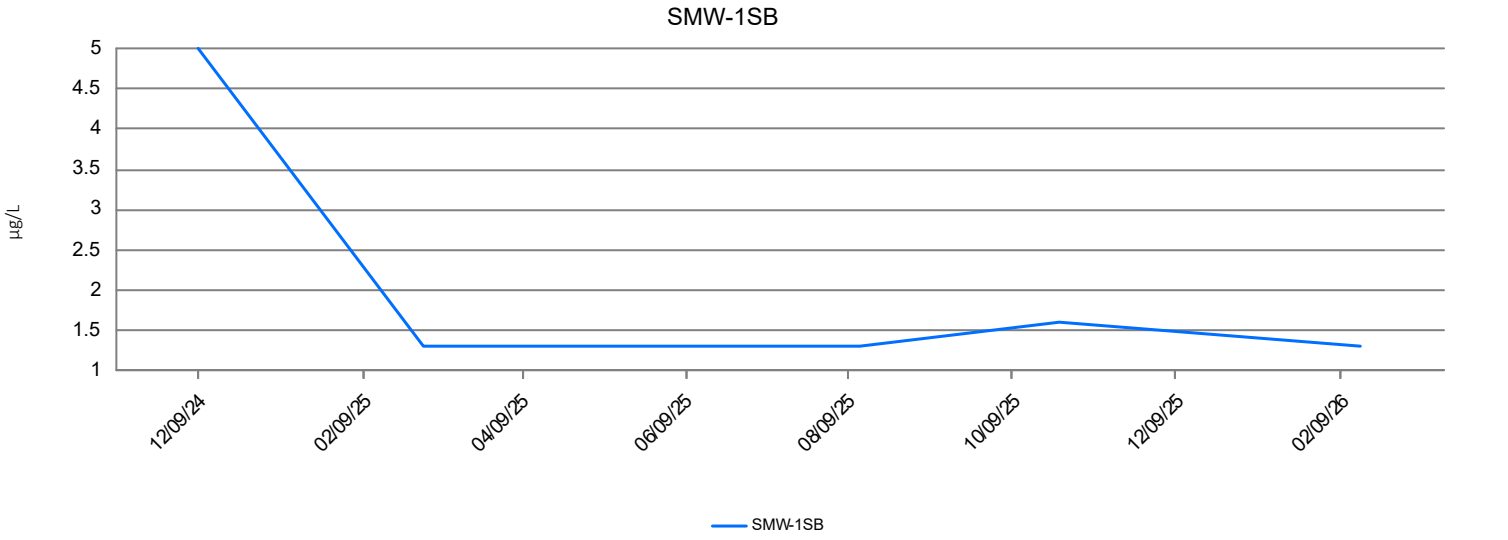
Variable Graphical Report

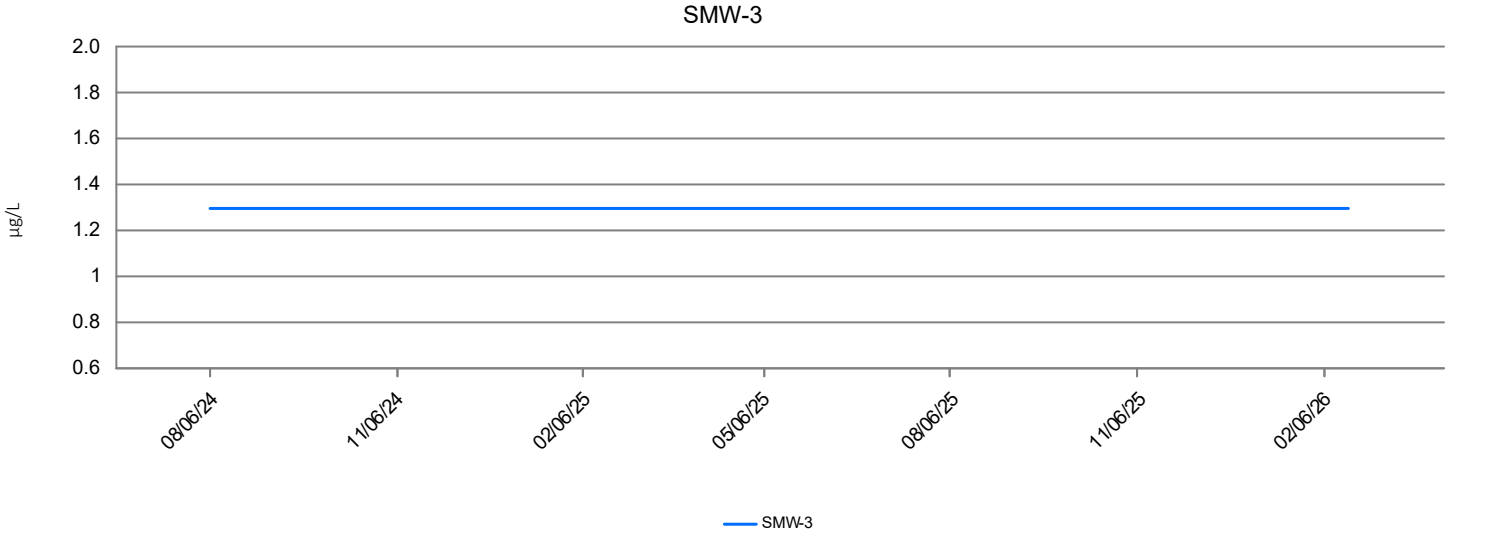
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Tin, Total Recoverable (µg/L)





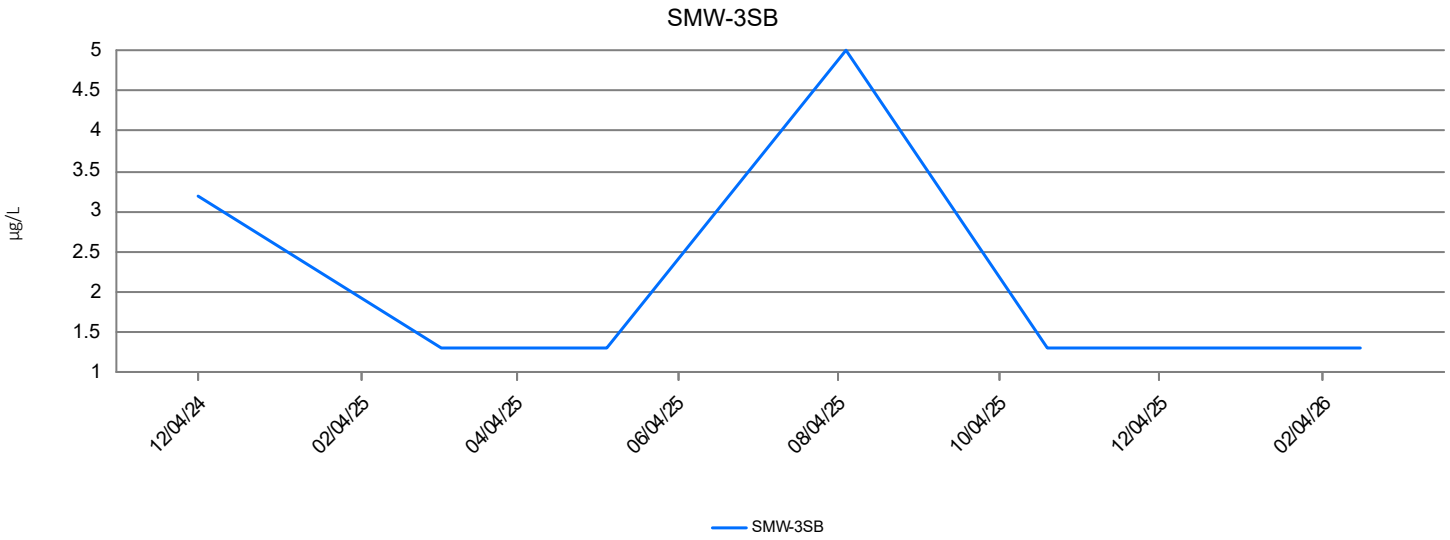


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Tin, Total Recoverable (µg/L)

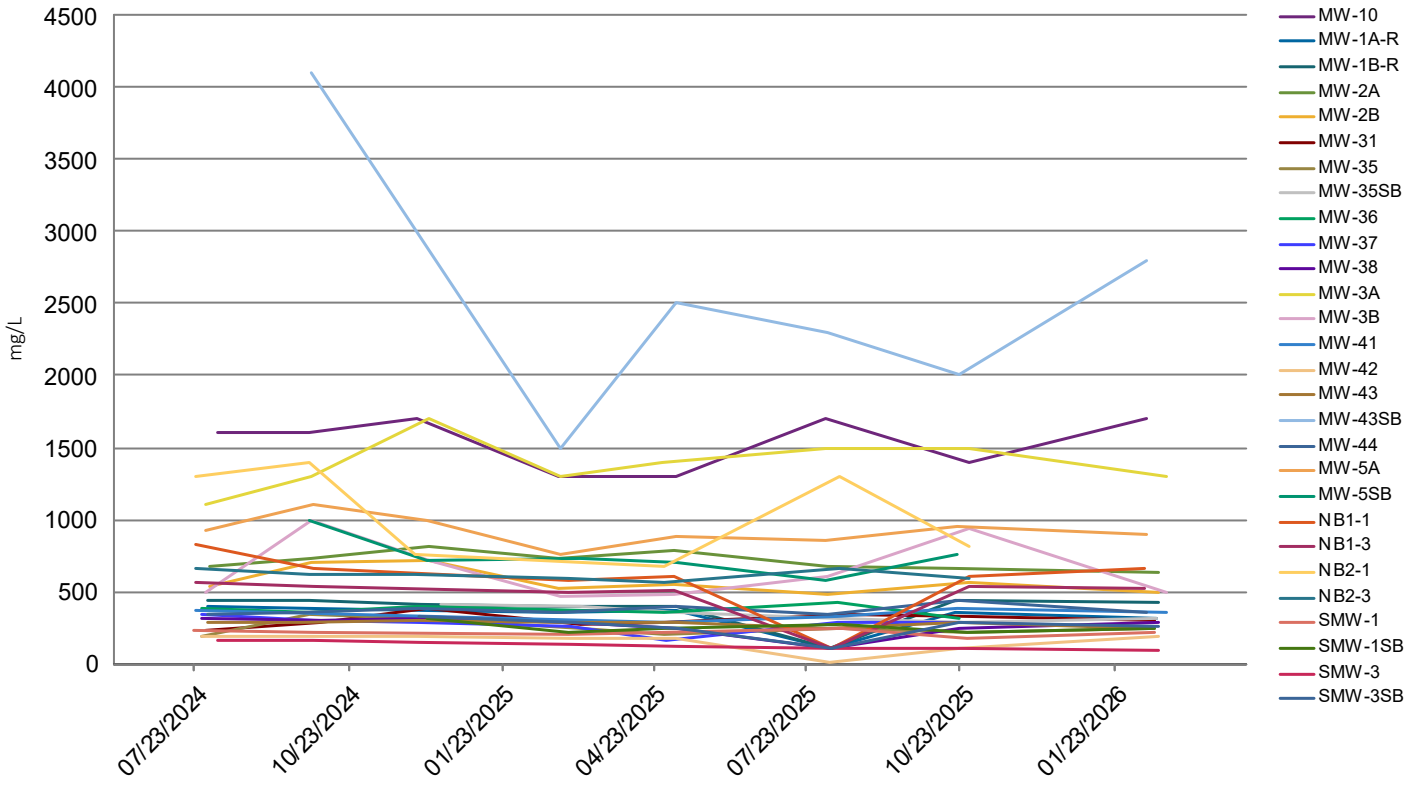


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Dissolved Solids (mg/L)

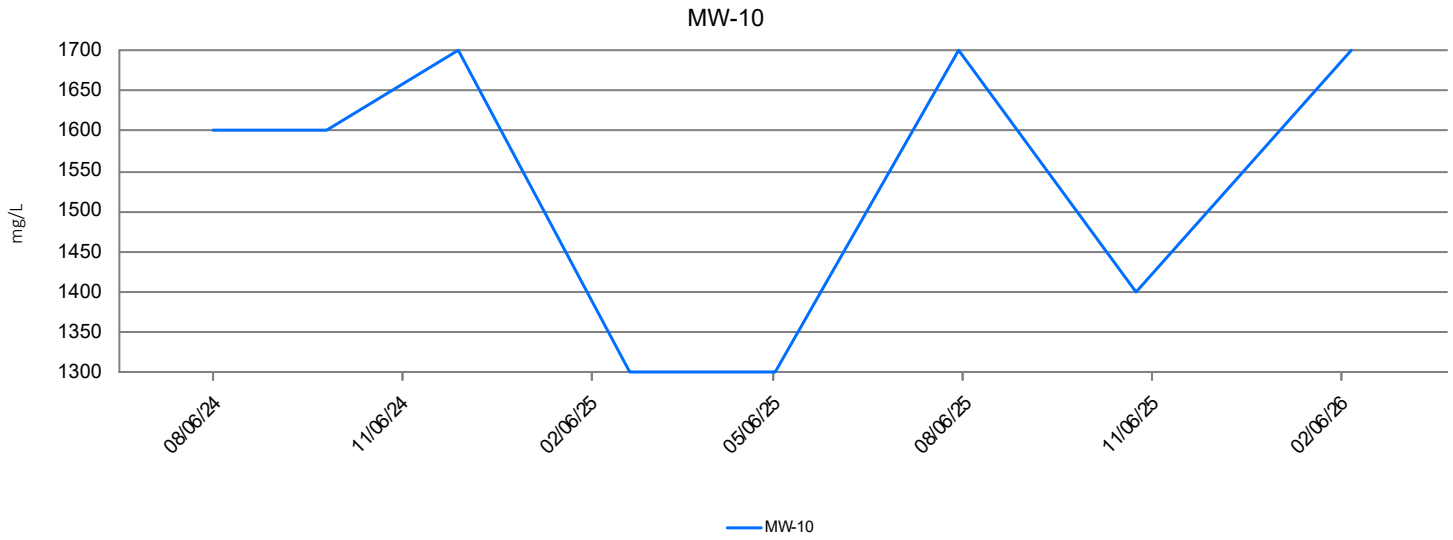


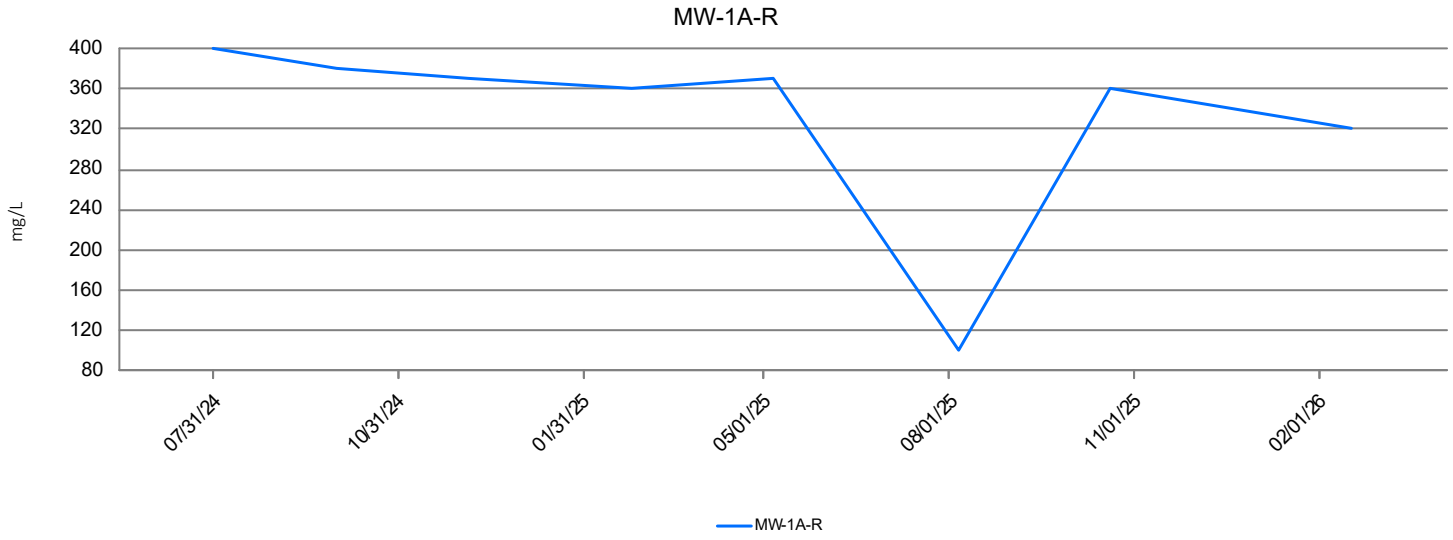
Variable Graphical Report

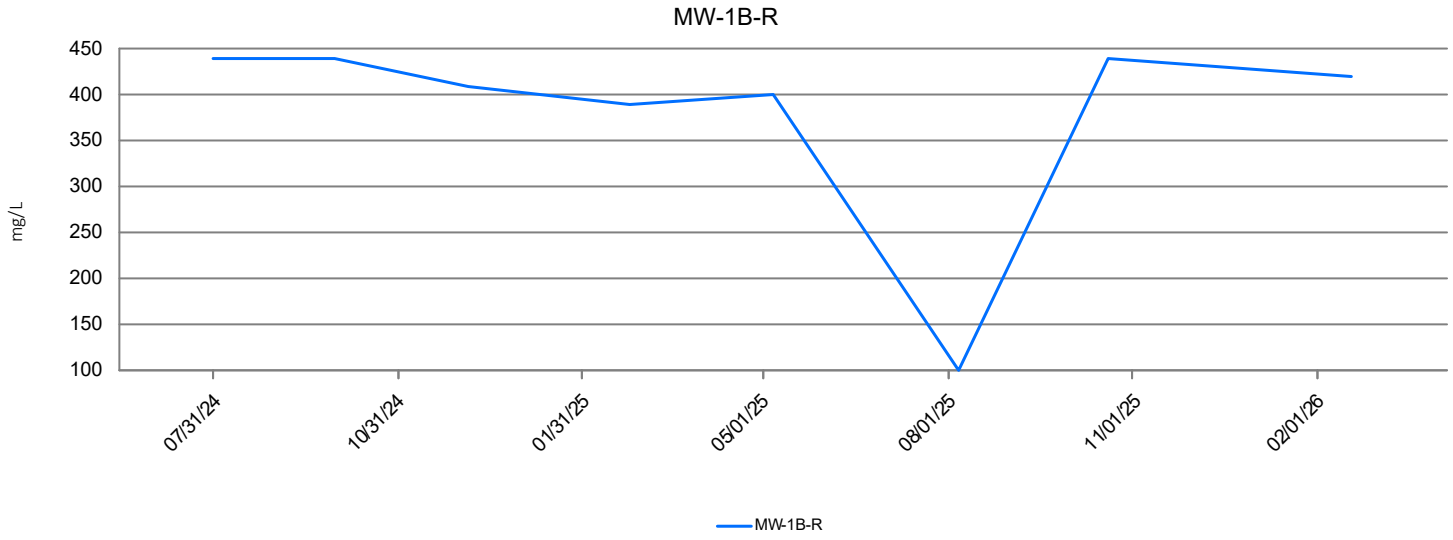
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Dissolved Solids (mg/L)







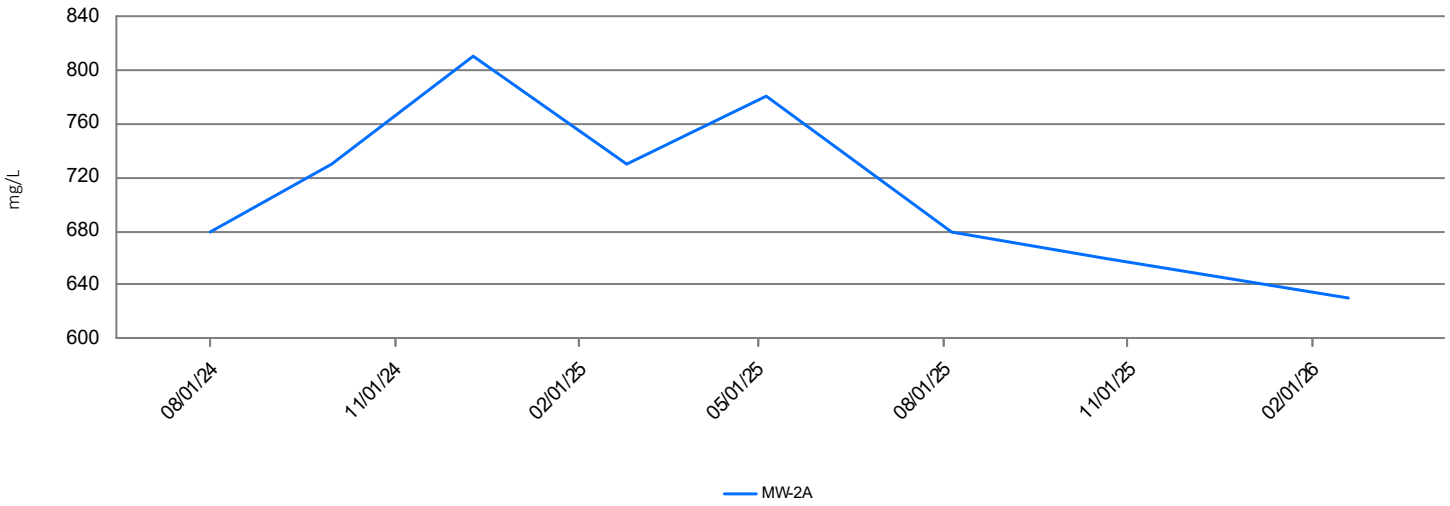
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

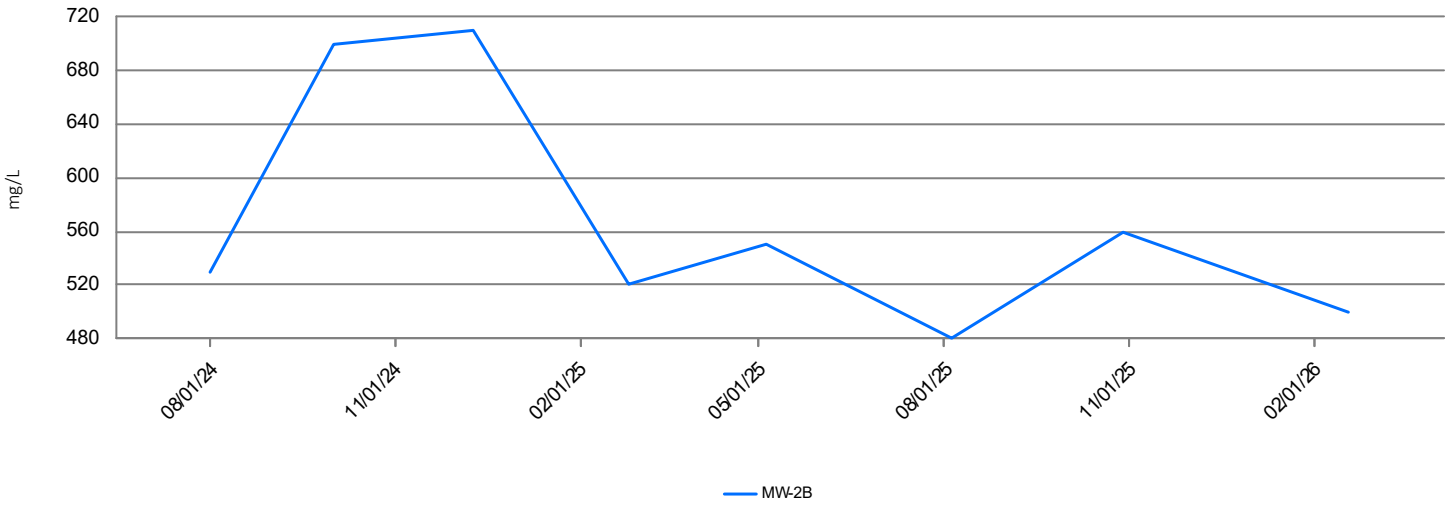
MonitorPro

No Group Selected, Total Dissolved Solids (mg/L)

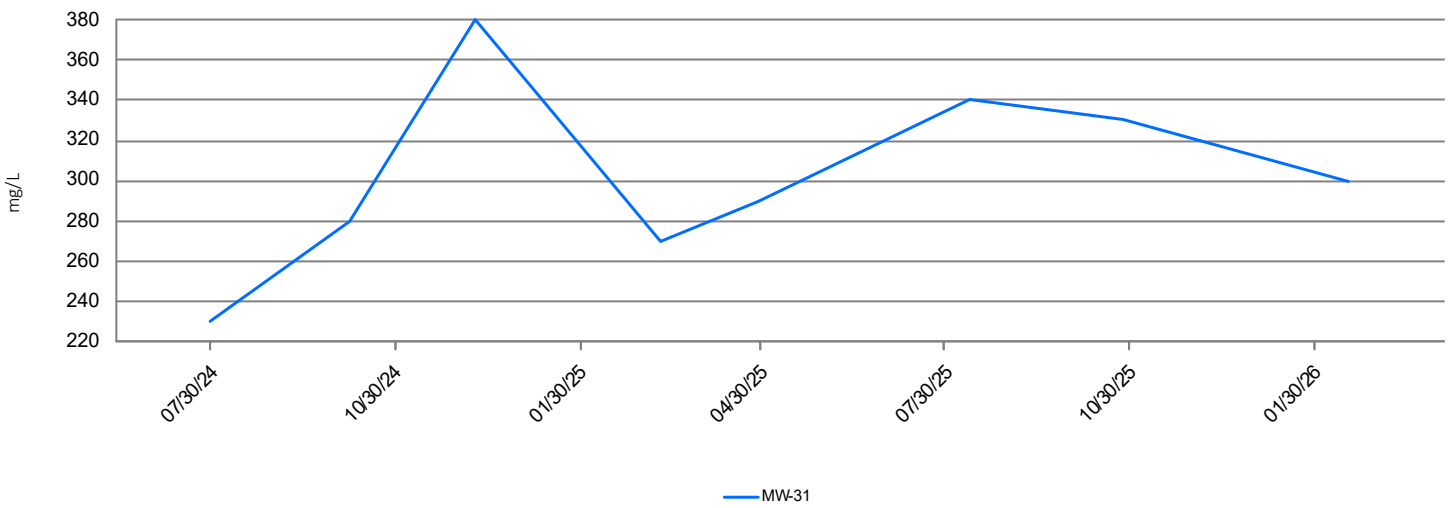
MW-2A



MW-2B



MW-31

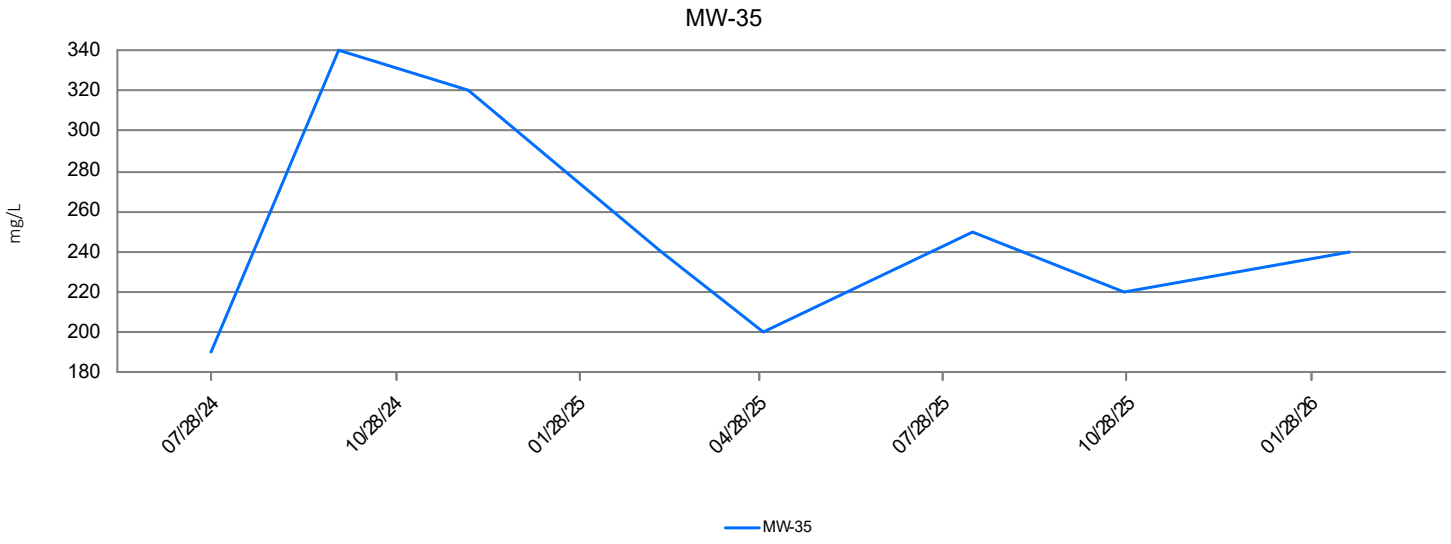


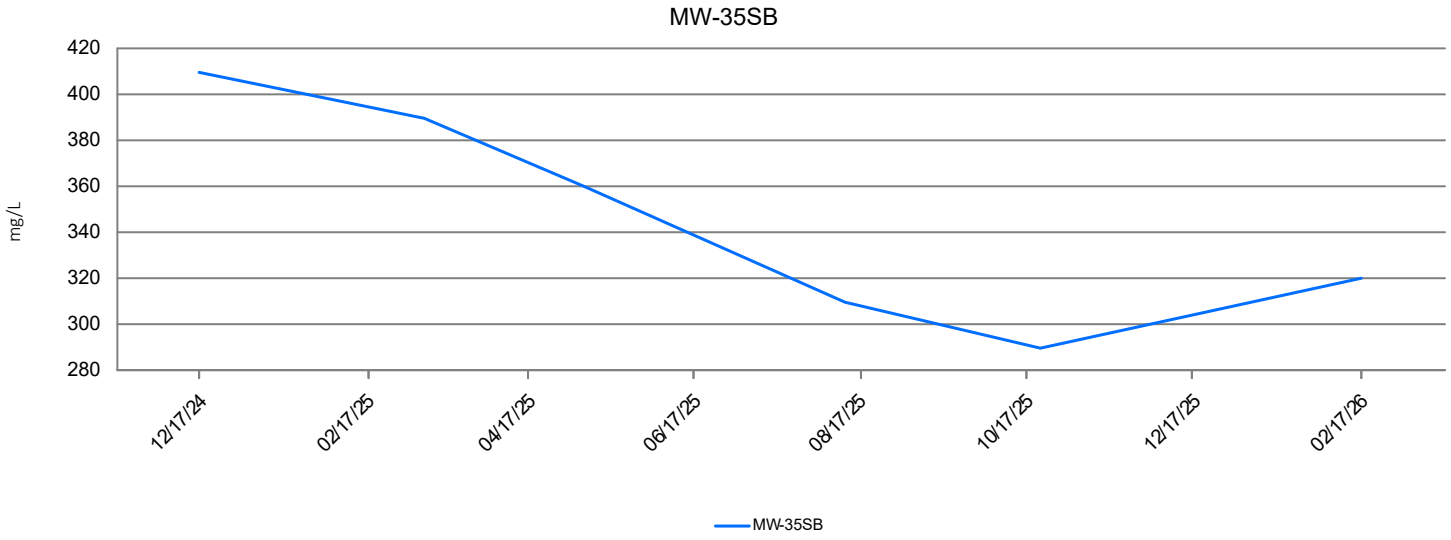
Variable Graphical Report

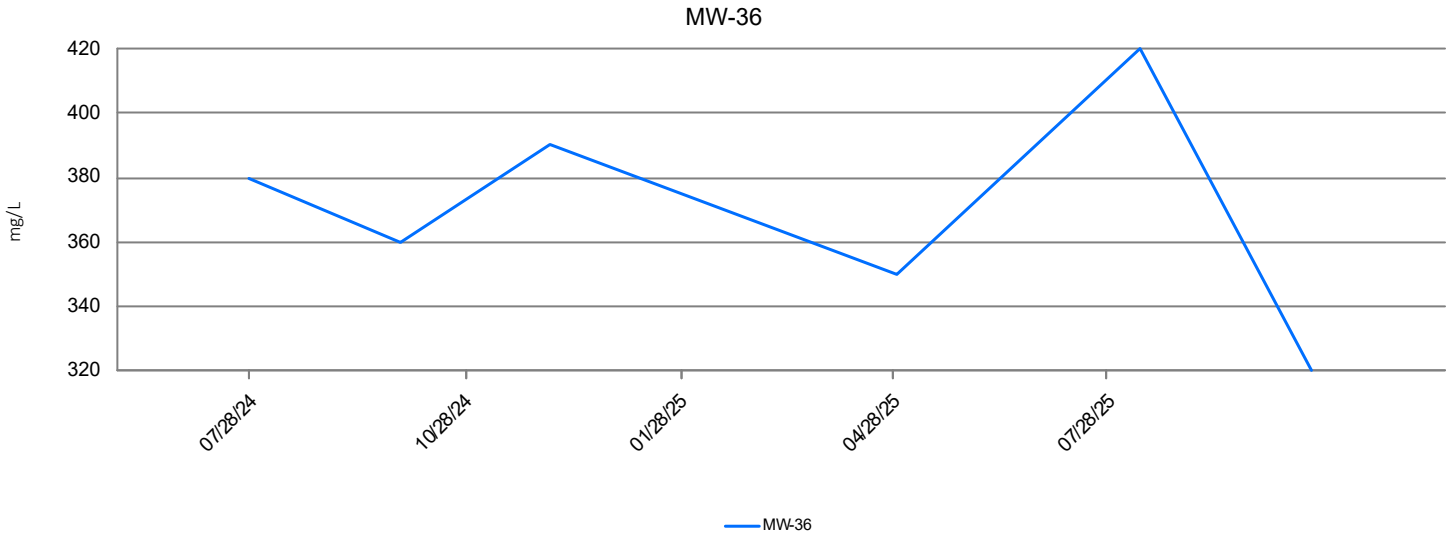
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Dissolved Solids (mg/L)







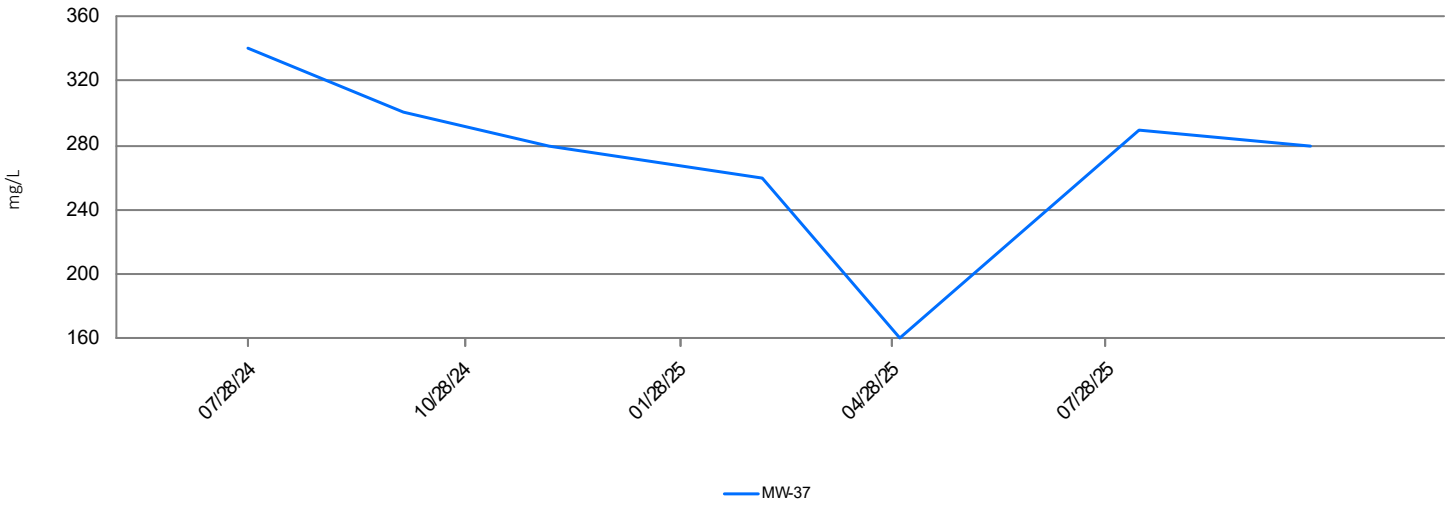
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

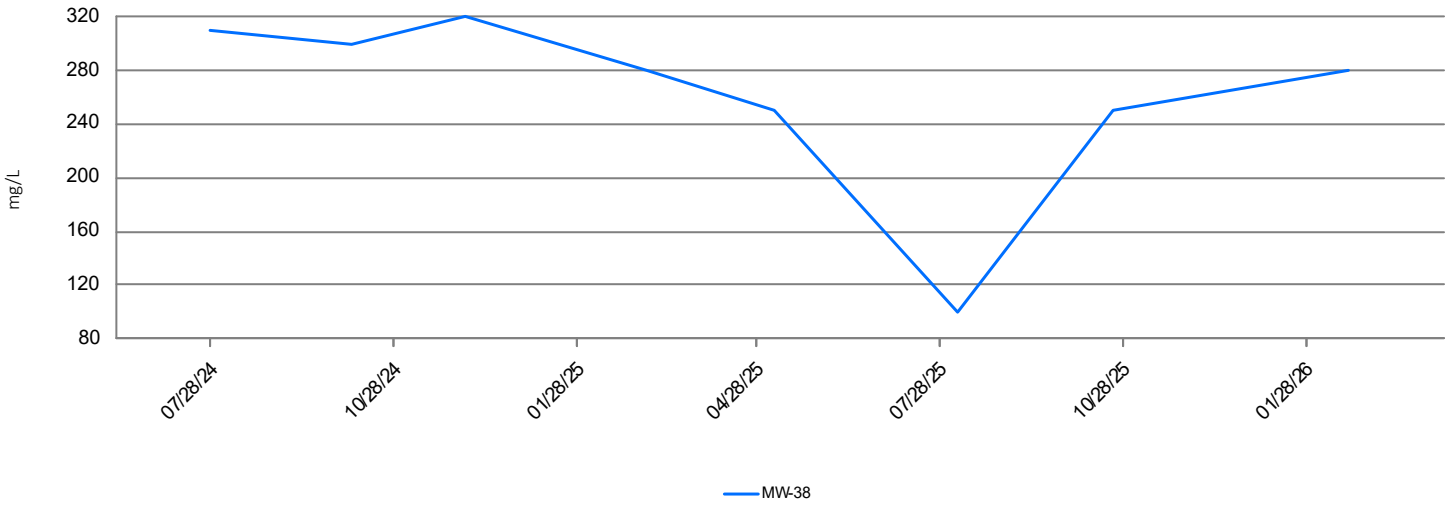
MonitorPro

No Group Selected, Total Dissolved Solids (mg/L)

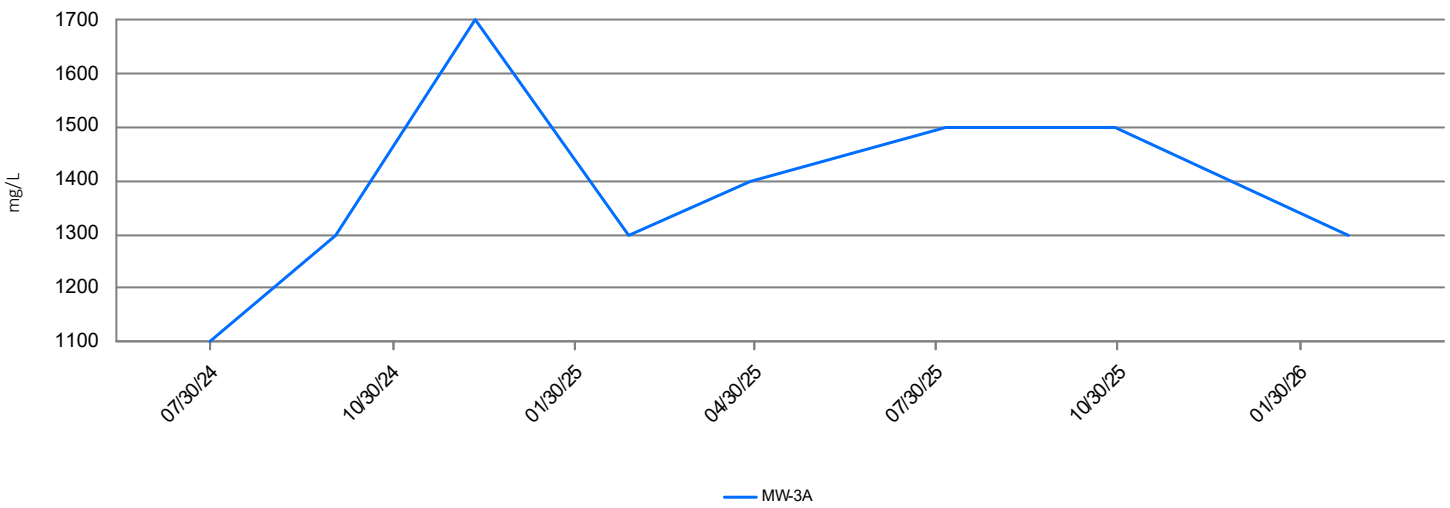
MW-37



MW-38



MW-3A

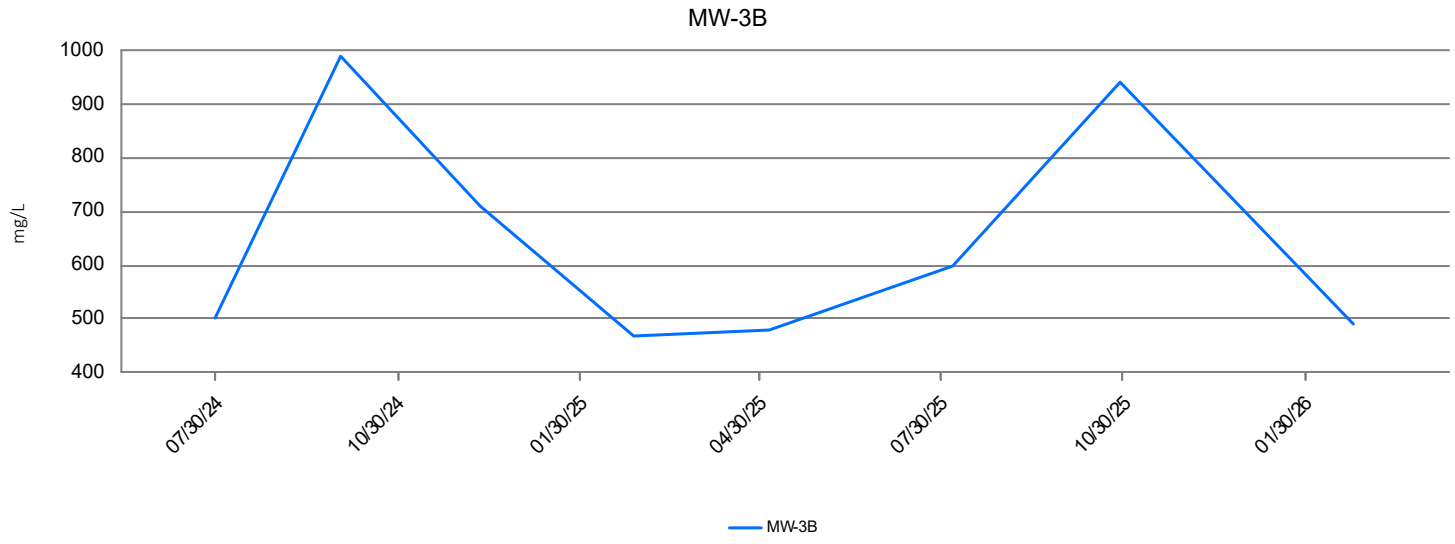


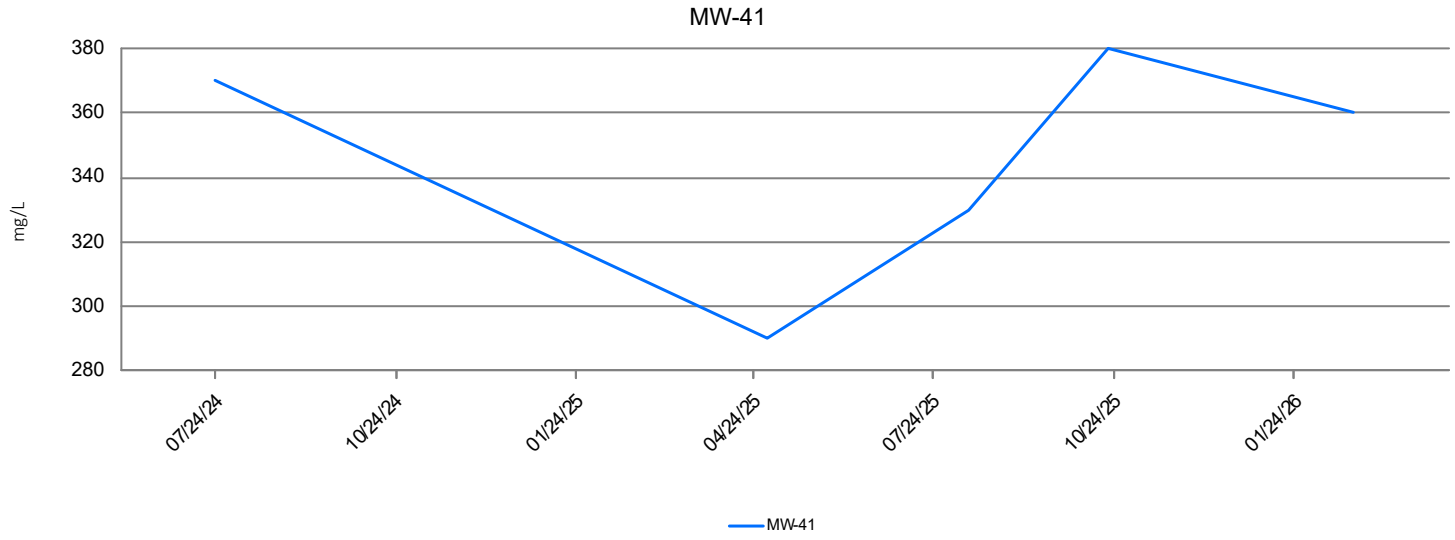
Variable Graphical Report

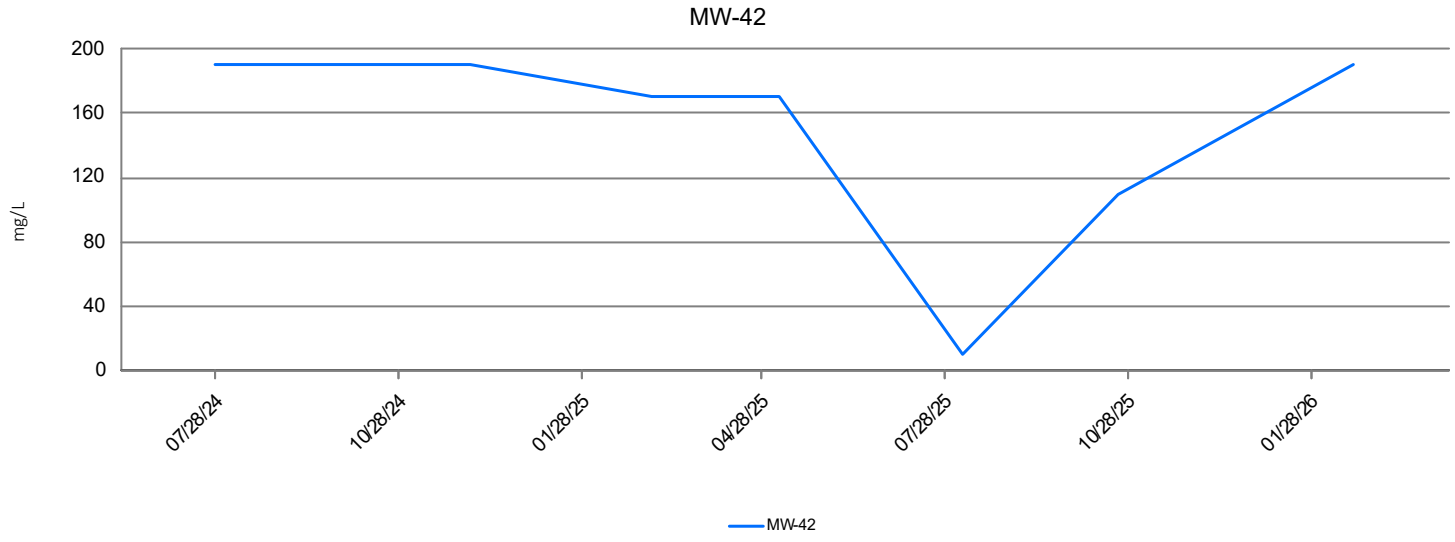
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Dissolved Solids (mg/L)





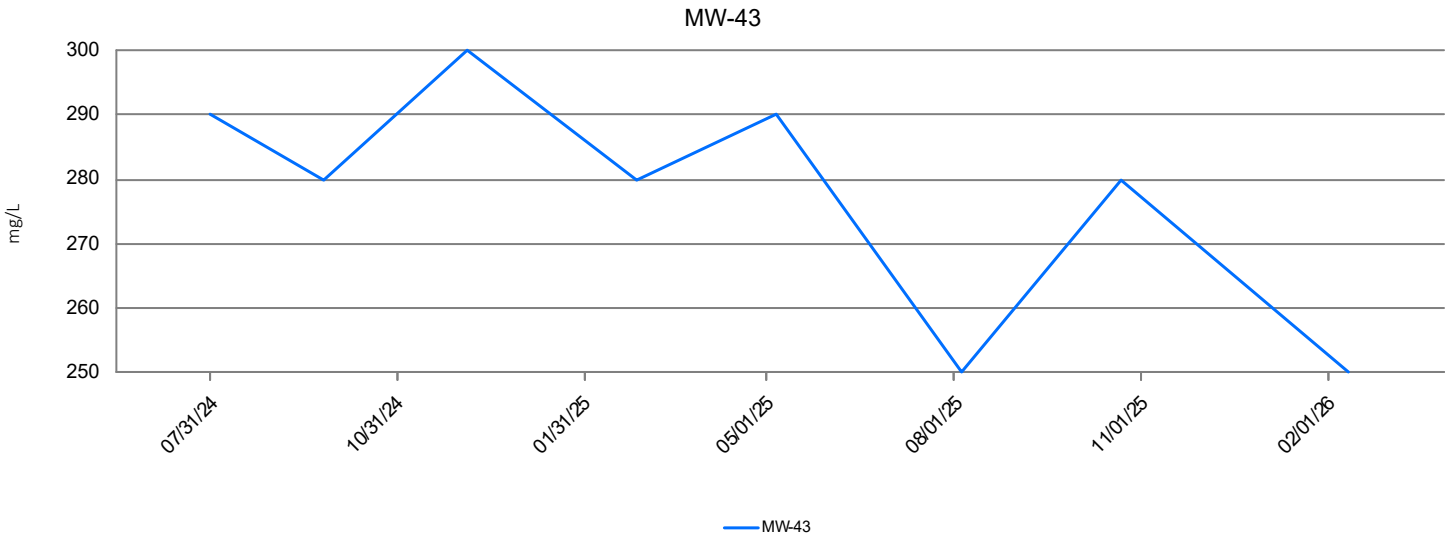


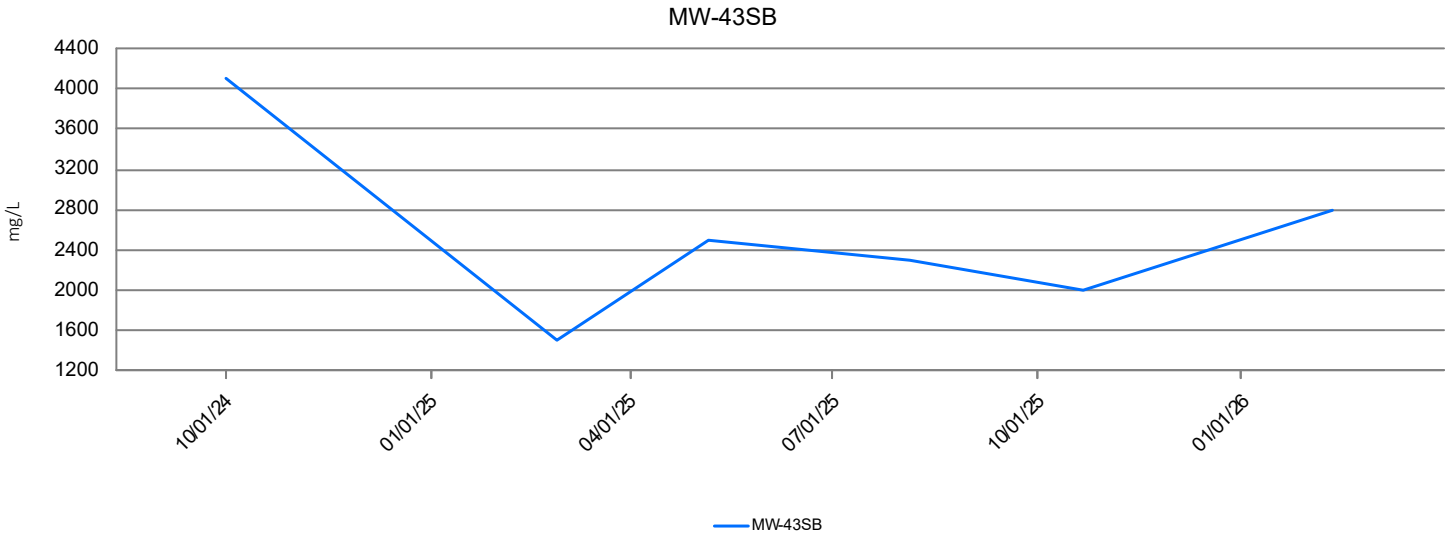
Variable Graphical Report

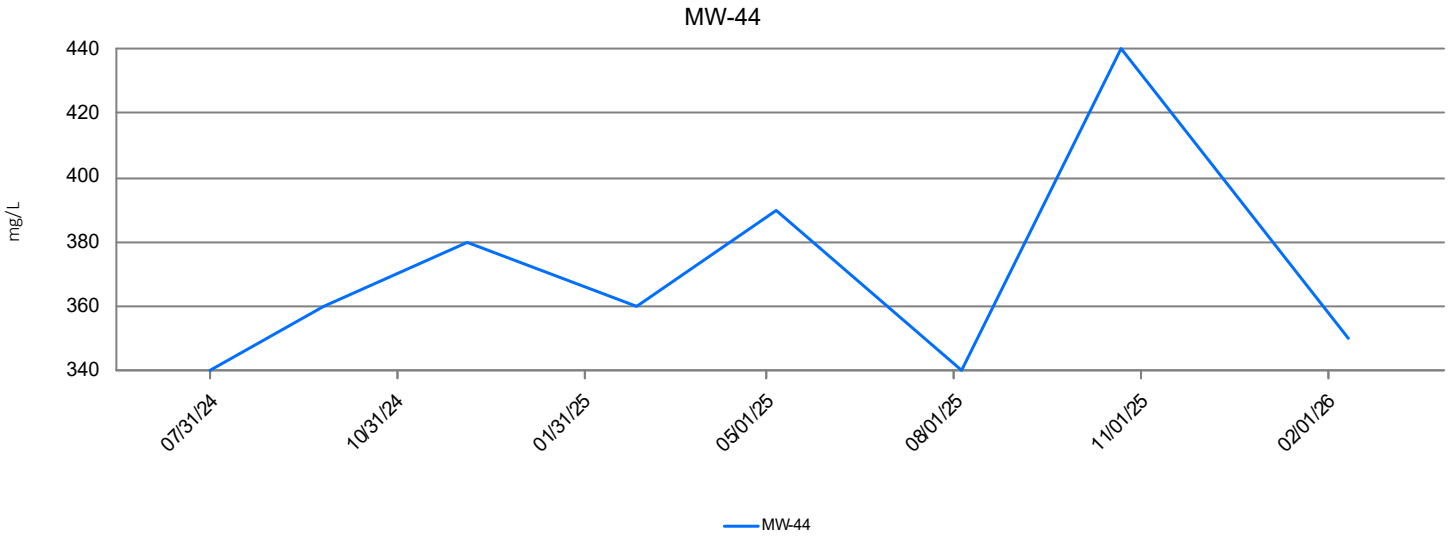
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Dissolved Solids (mg/L)





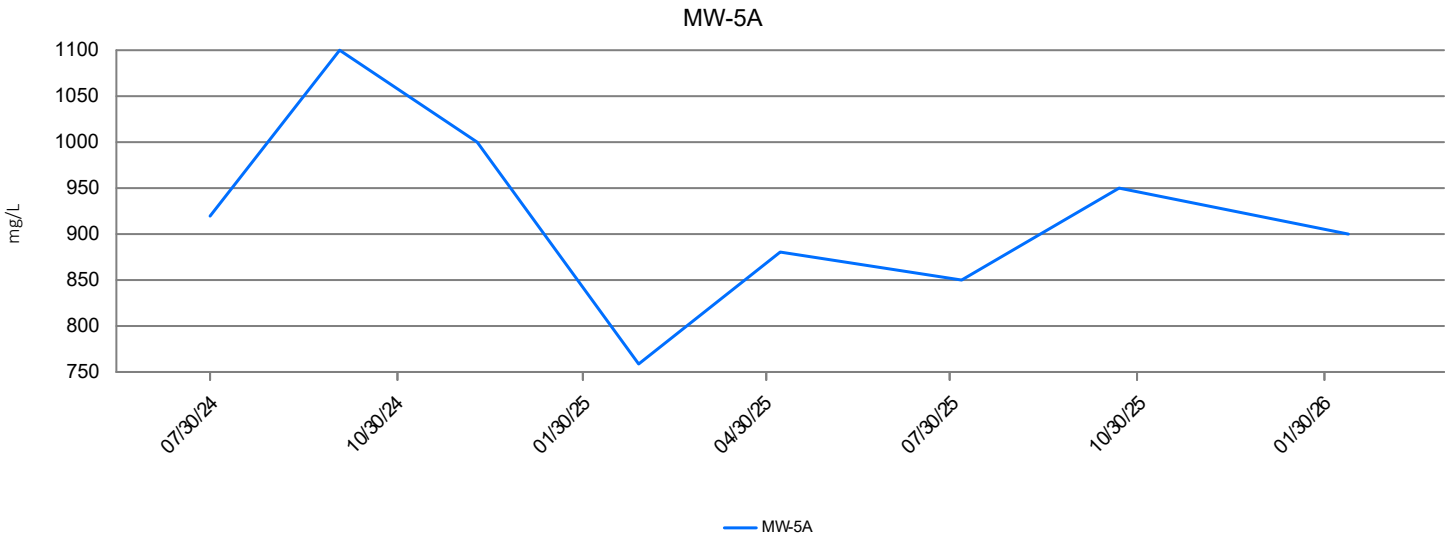


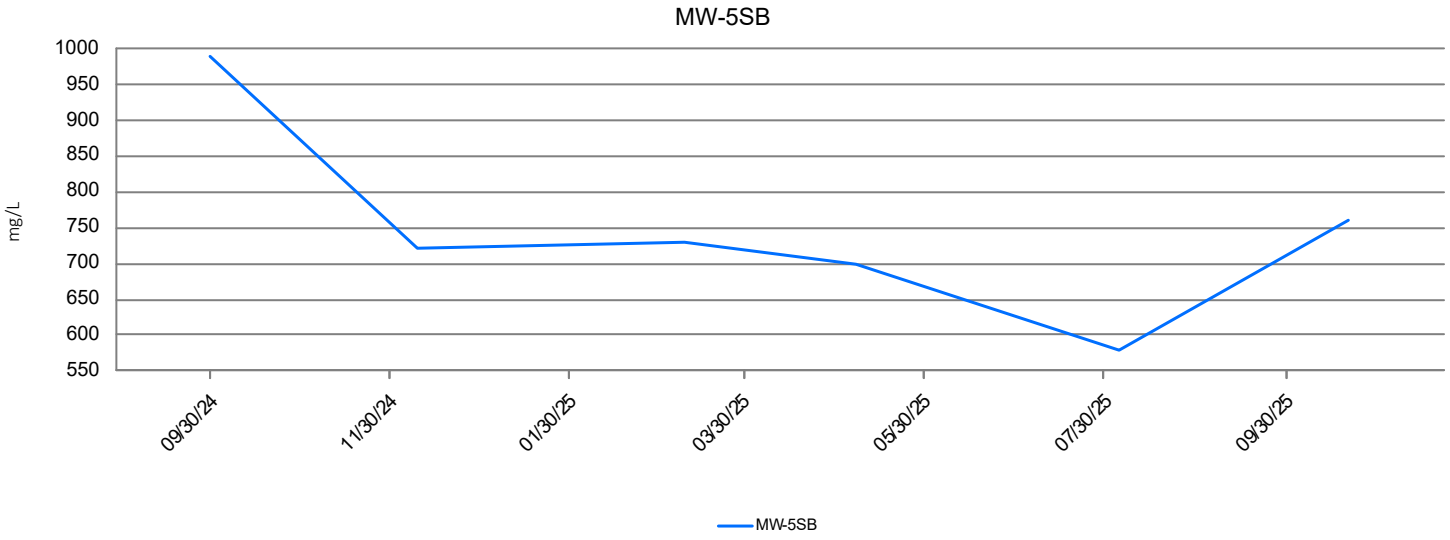
Variable Graphical Report

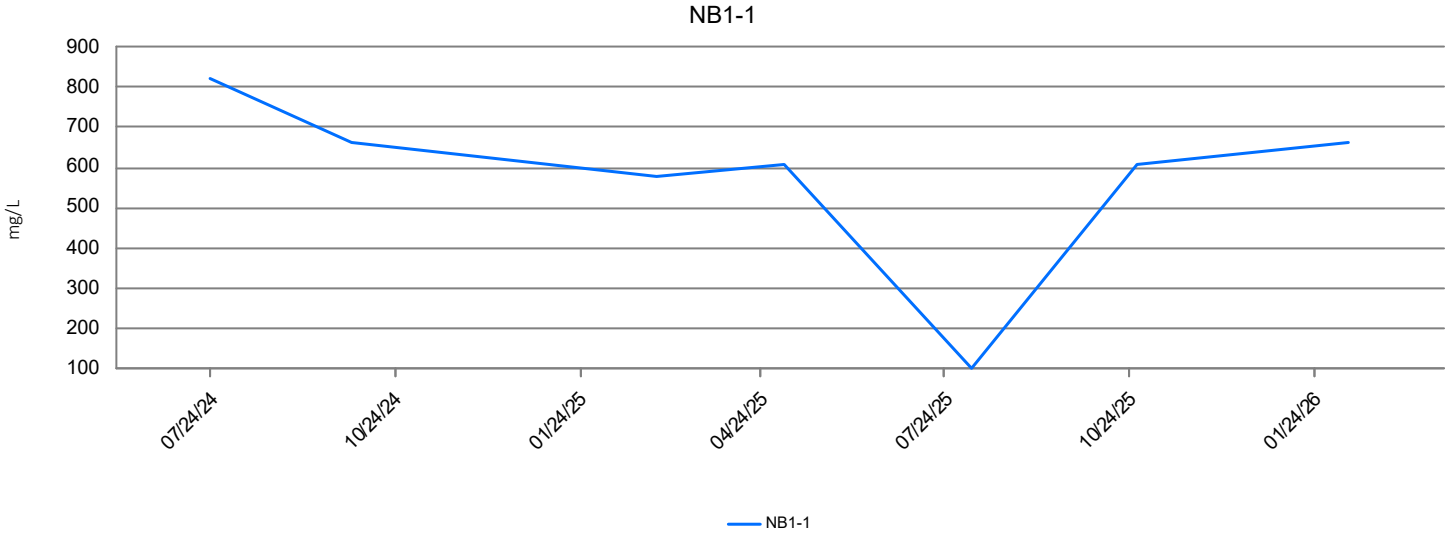
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Dissolved Solids (mg/L)





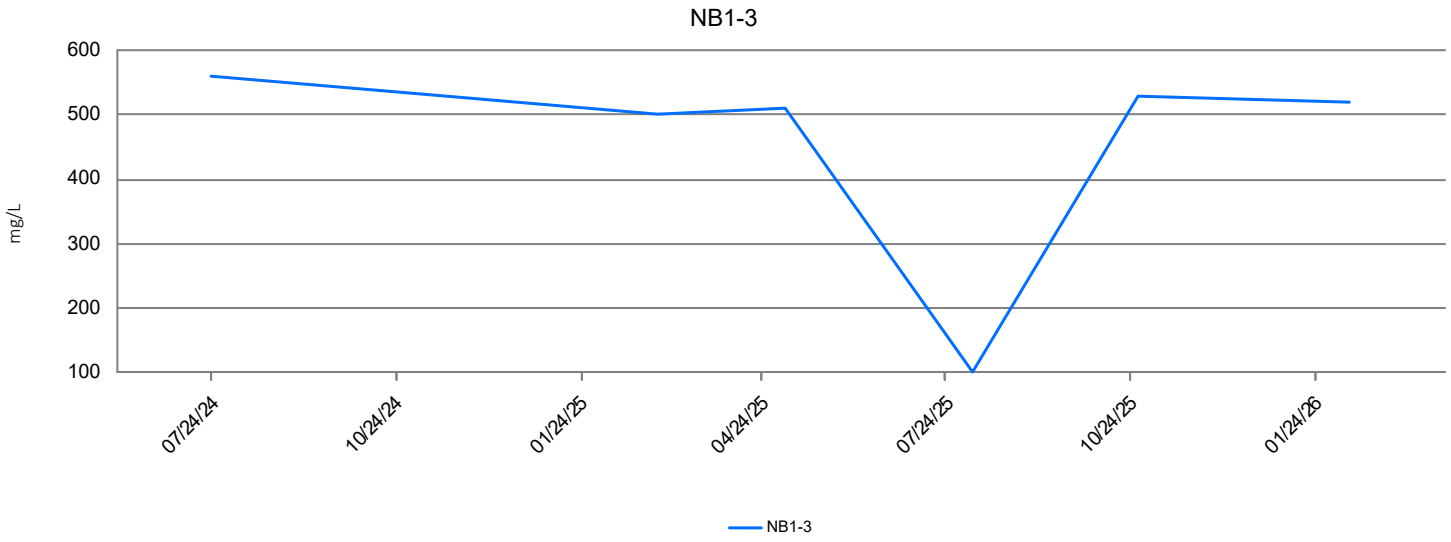


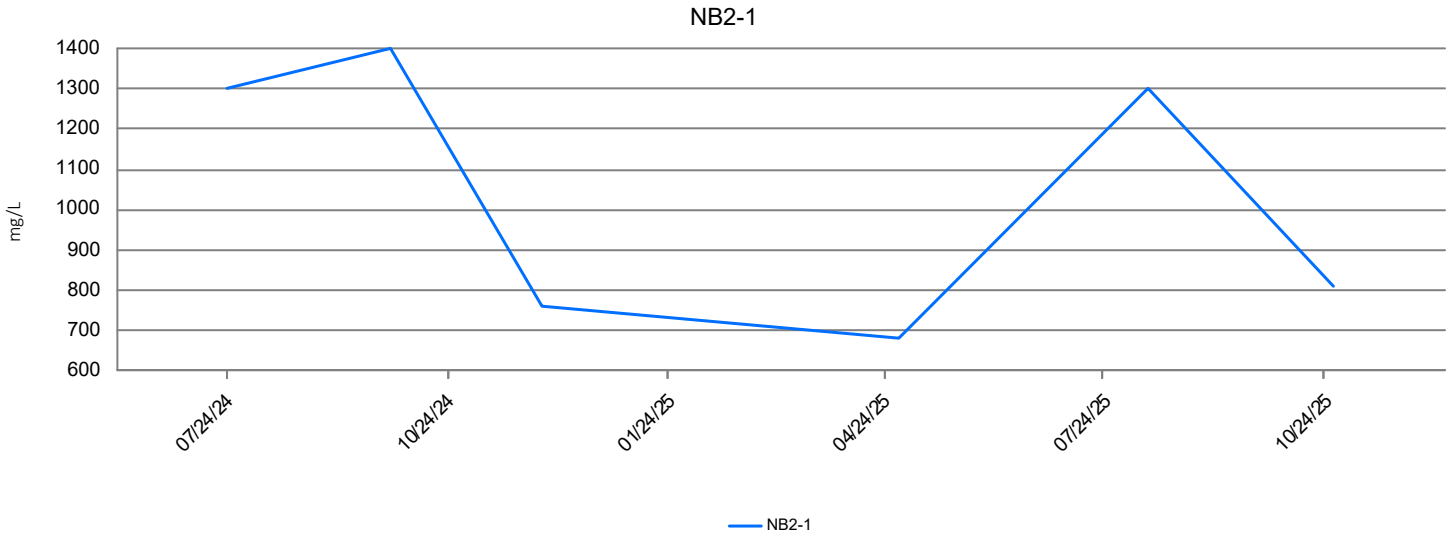
Variable Graphical Report

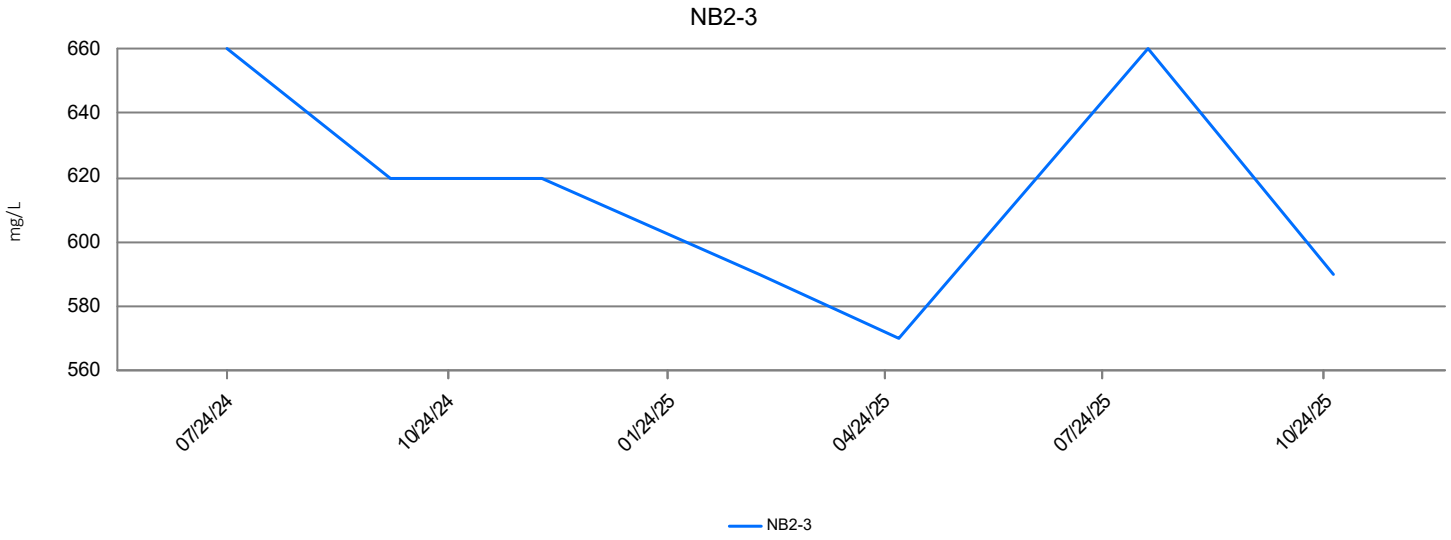
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Dissolved Solids (mg/L)





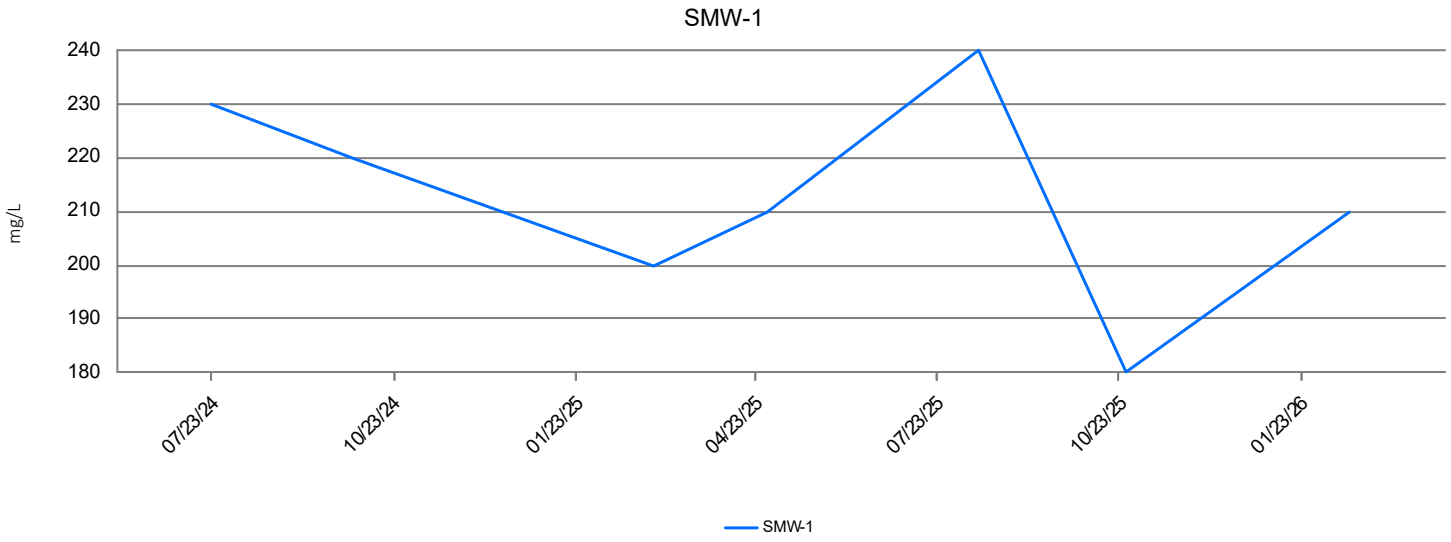


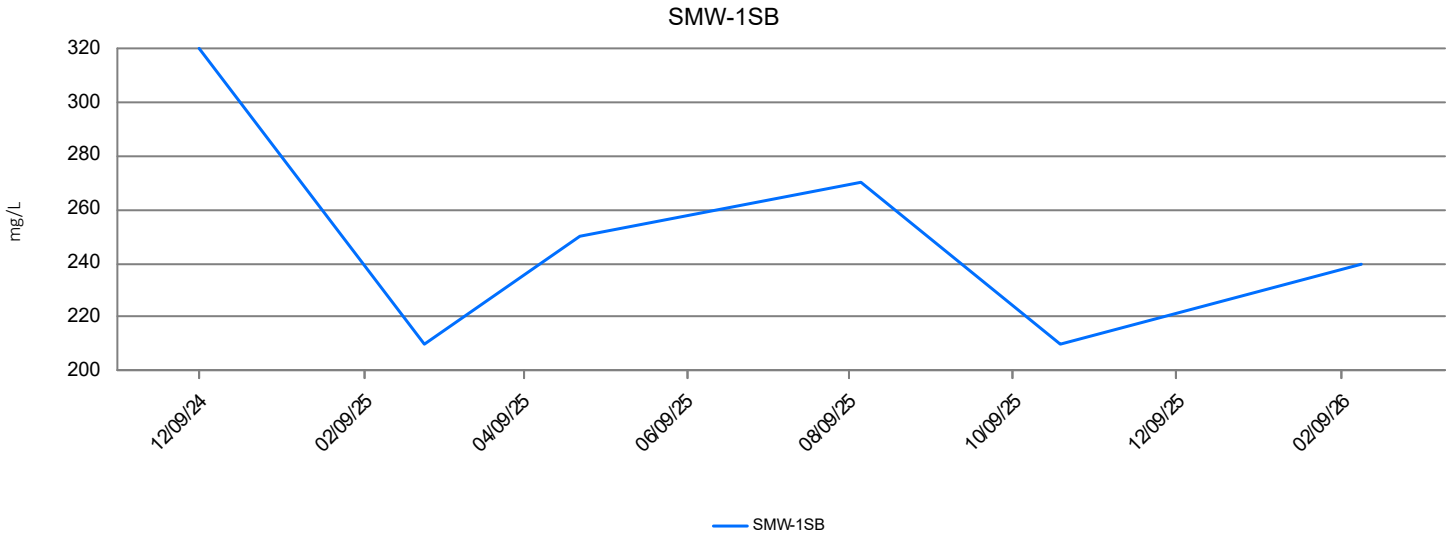
Variable Graphical Report

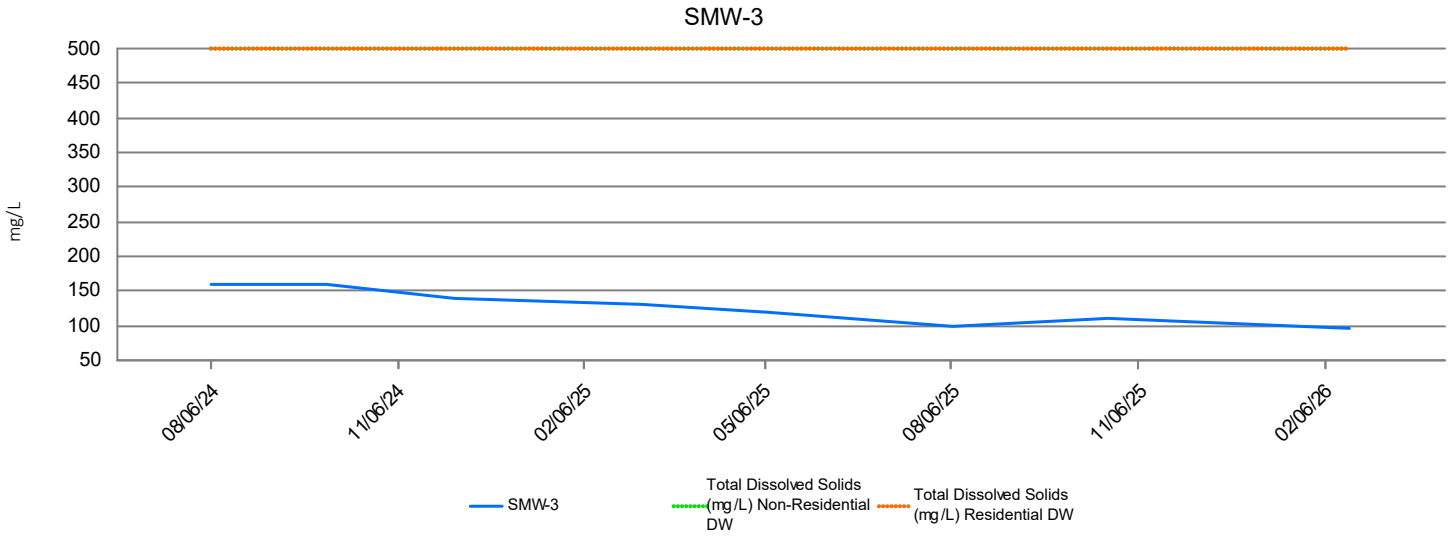
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Dissolved Solids (mg/L)





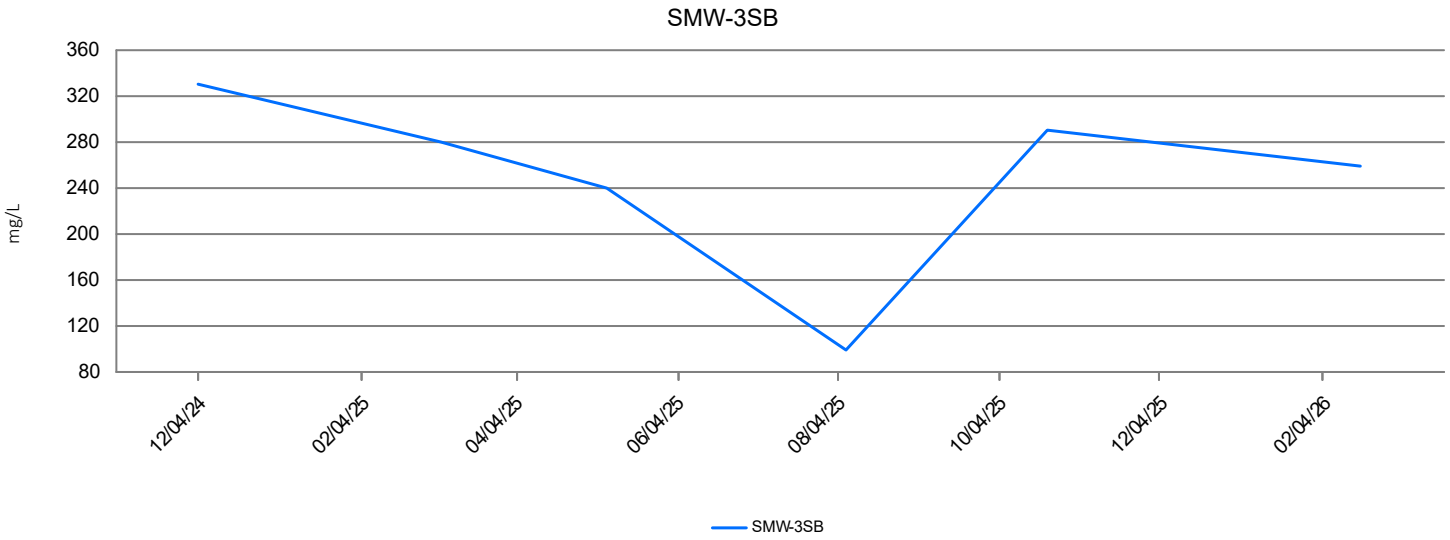


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Dissolved Solids (mg/L)

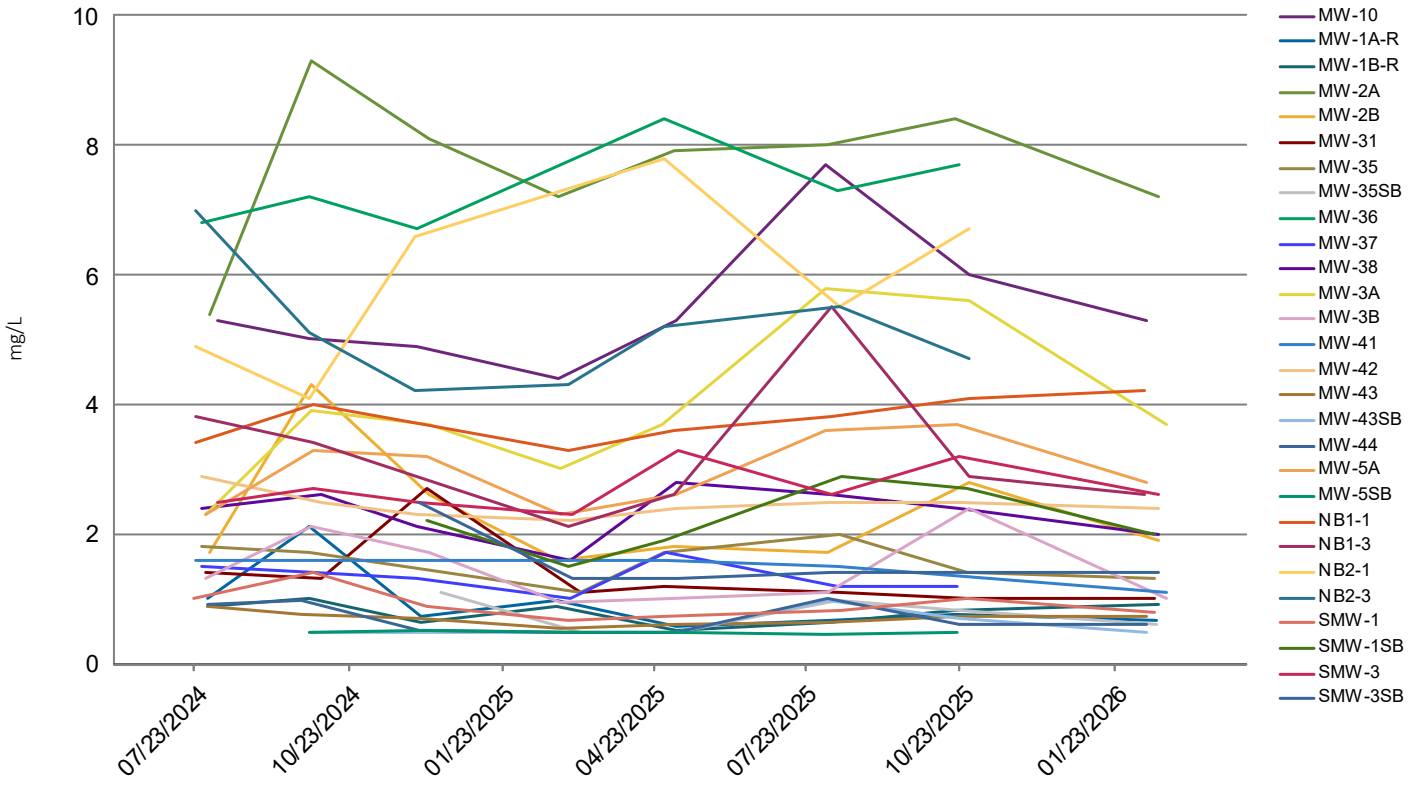


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Organic Carbon (TOC) (mg/L)

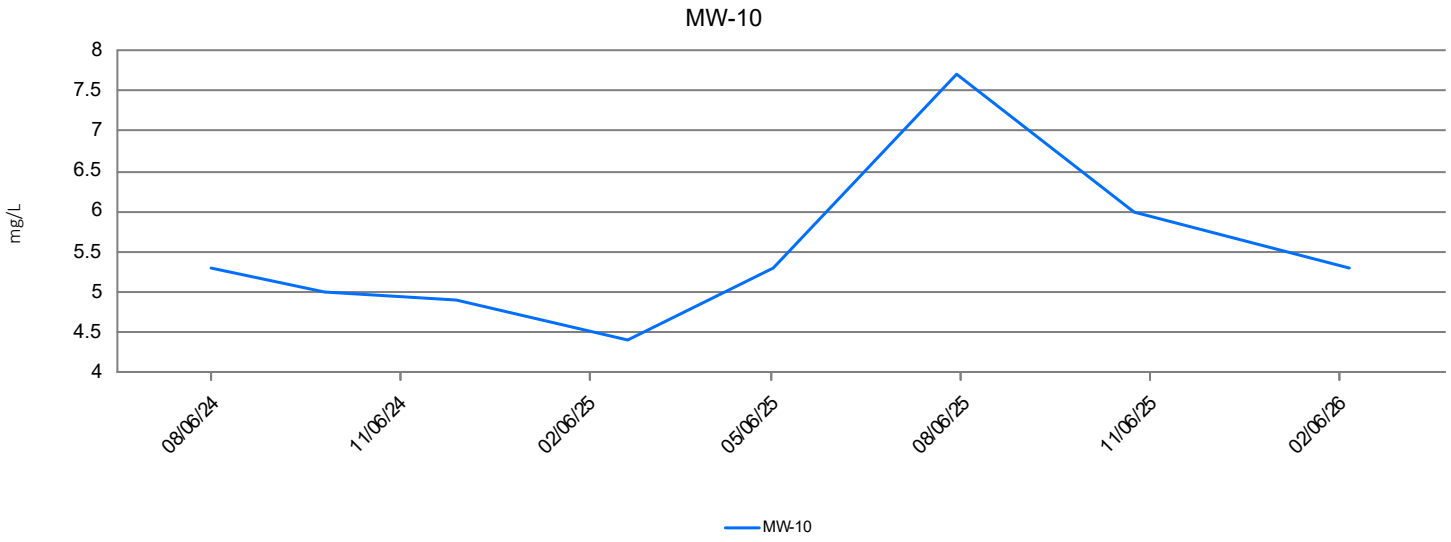


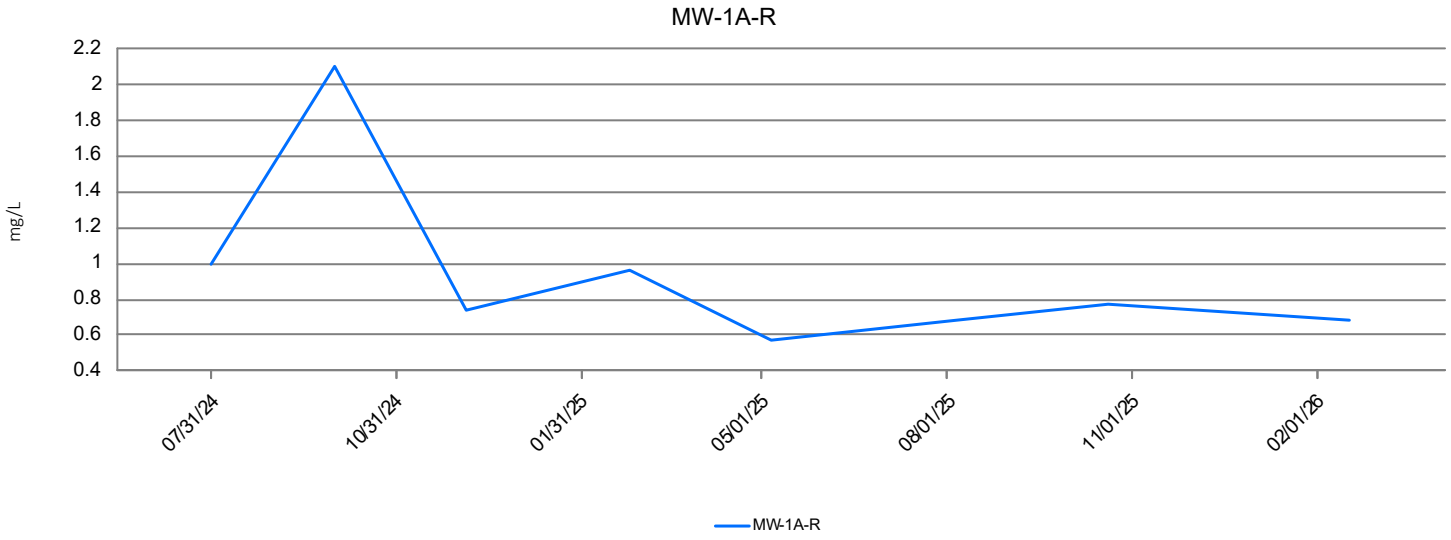
Variable Graphical Report

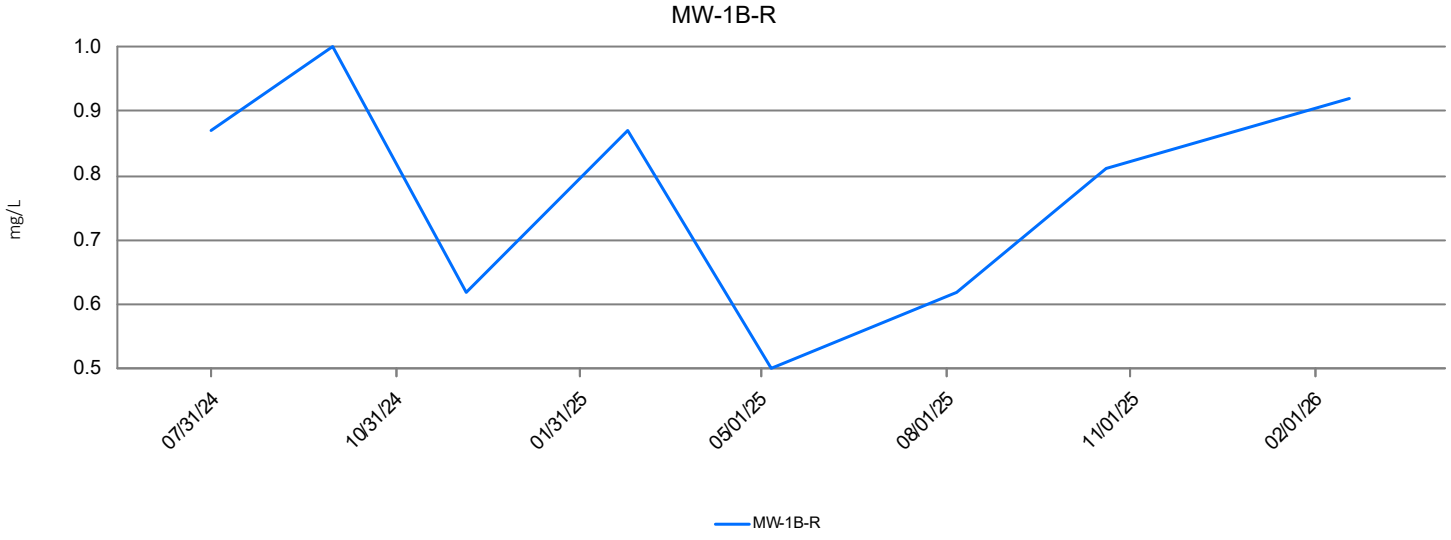
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Organic Carbon (TOC) (mg/L)





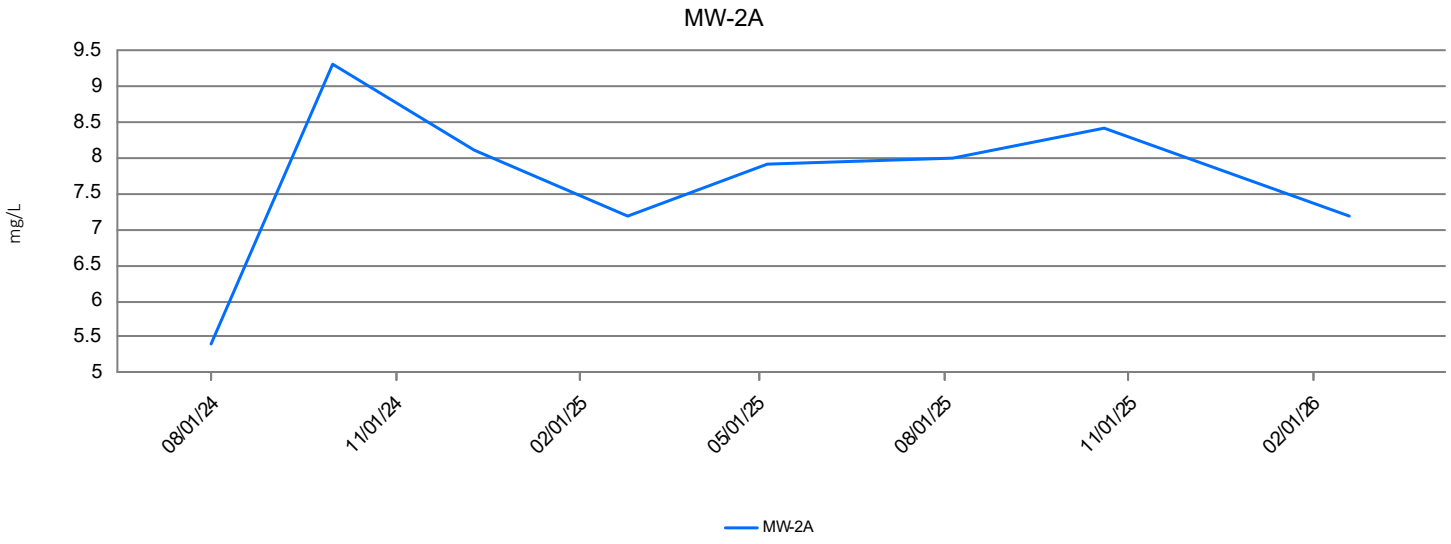


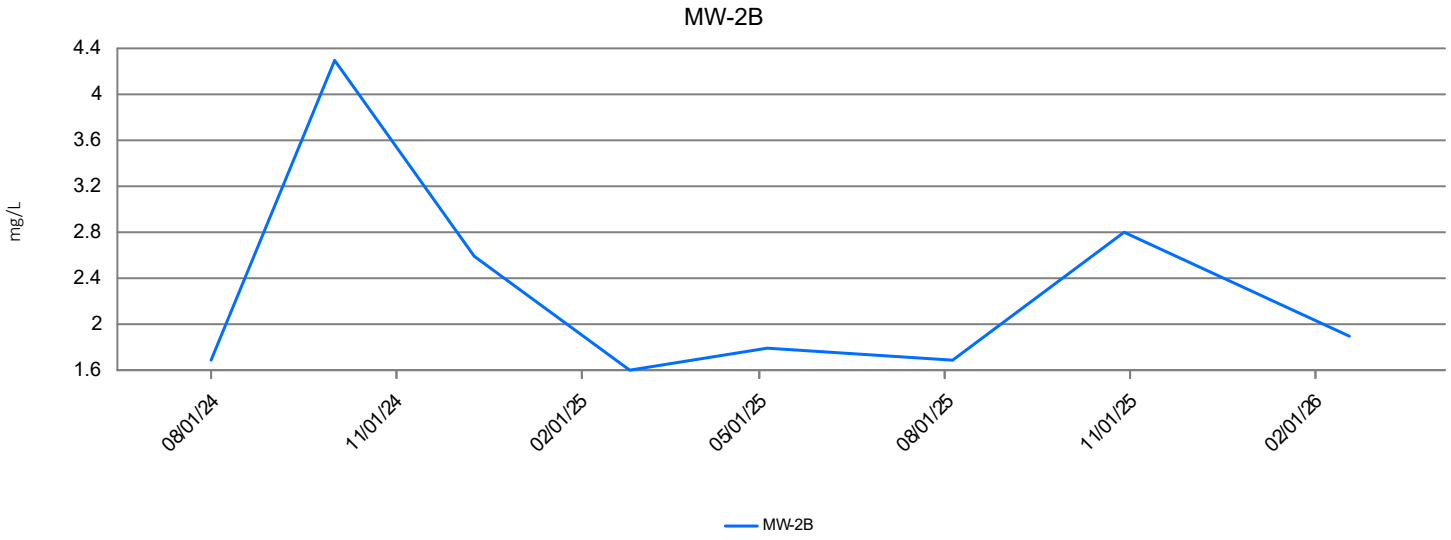
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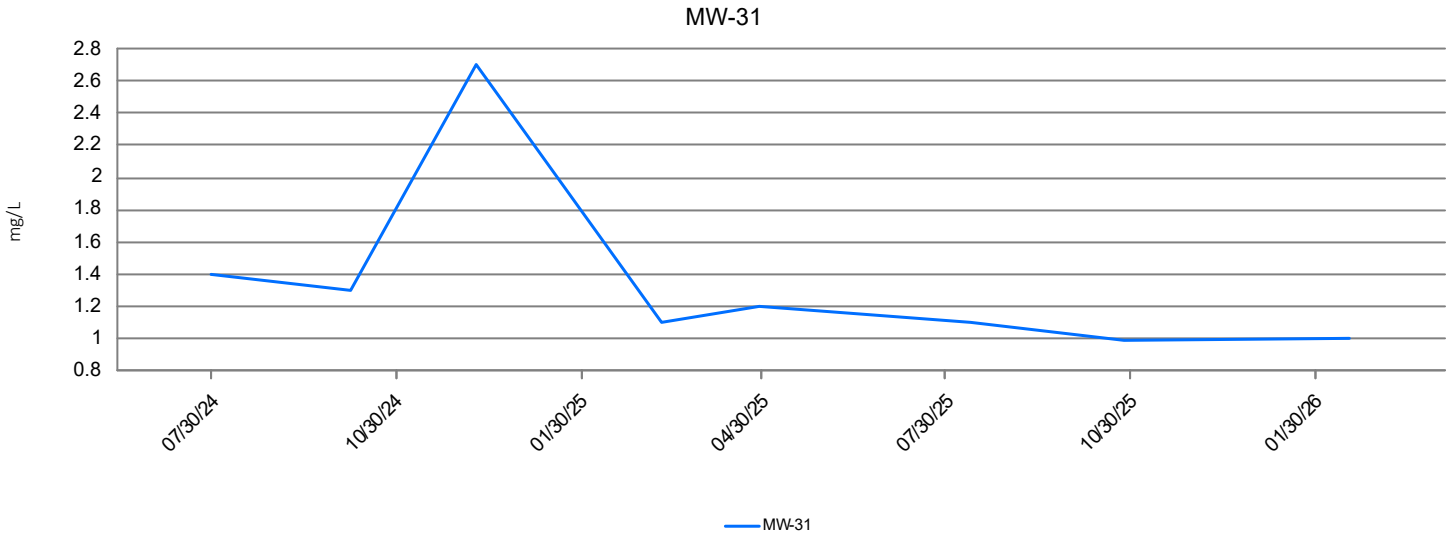
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Organic Carbon (TOC) (mg/L)





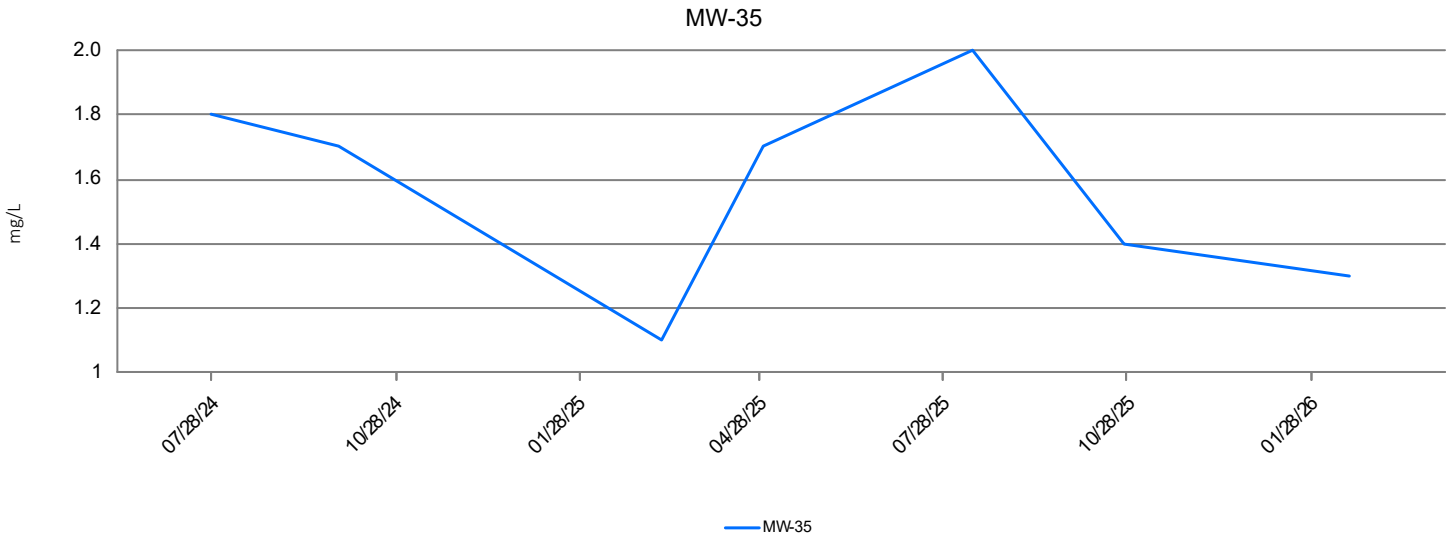


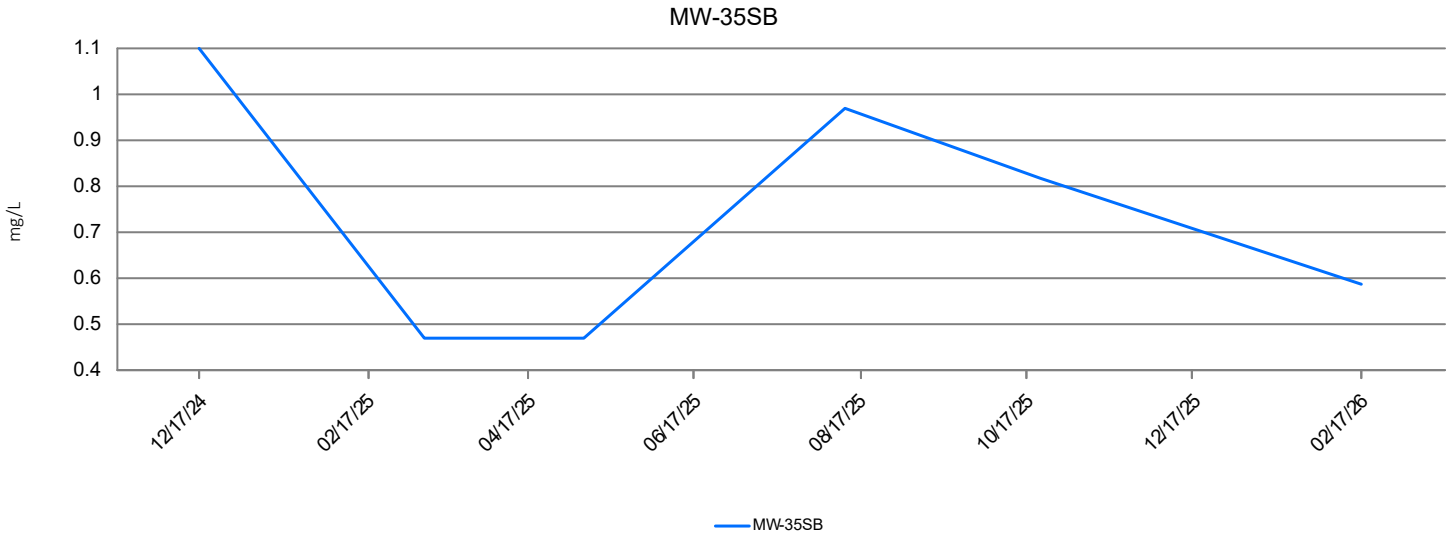
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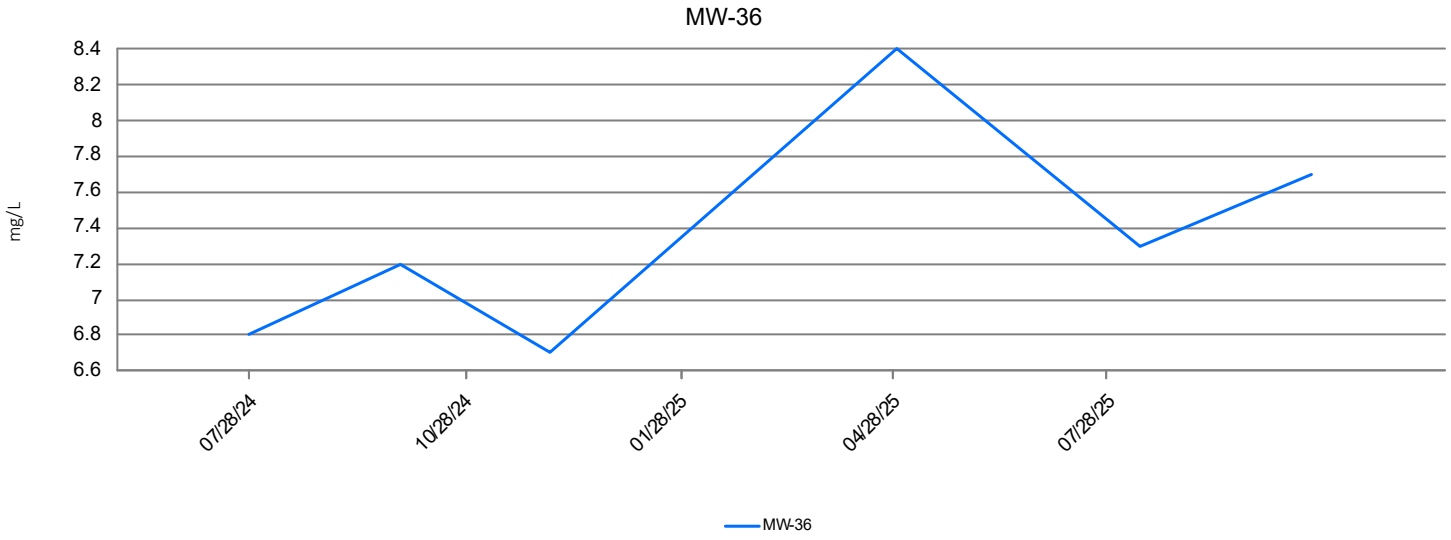
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Organic Carbon (TOC) (mg/L)





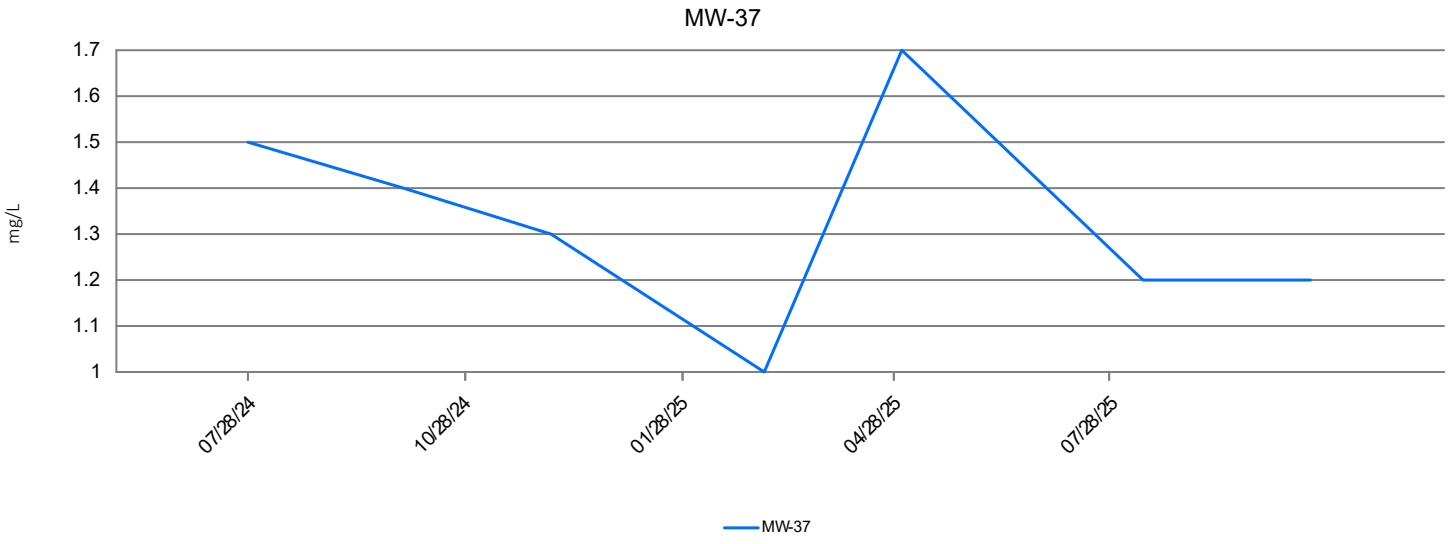


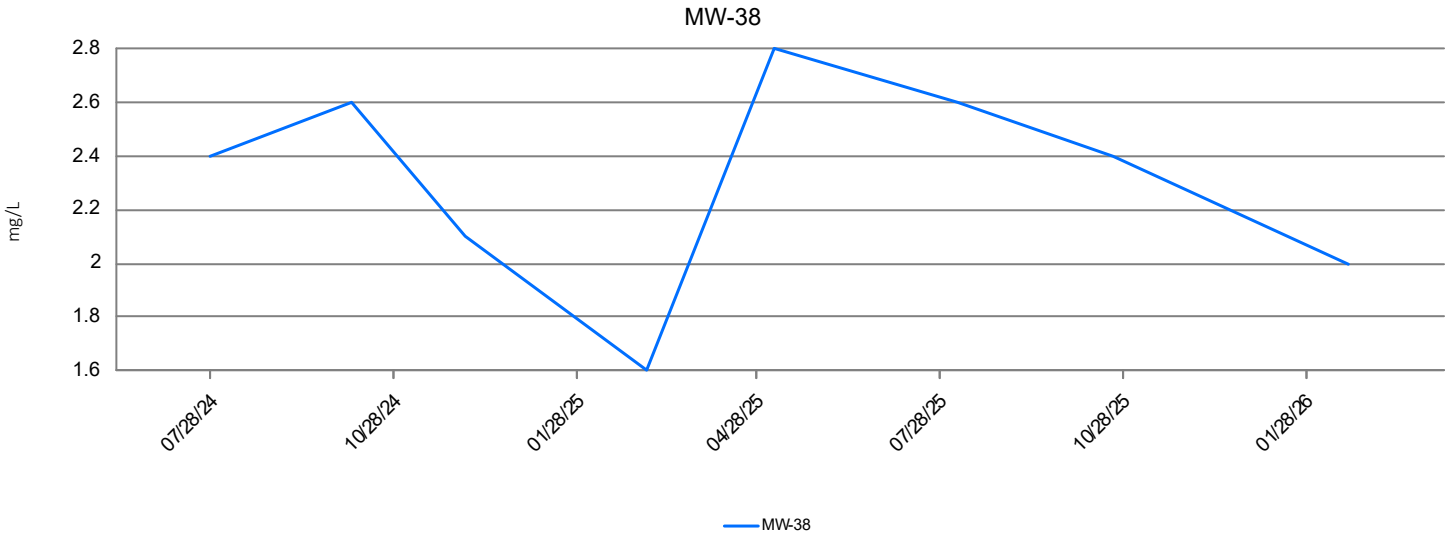
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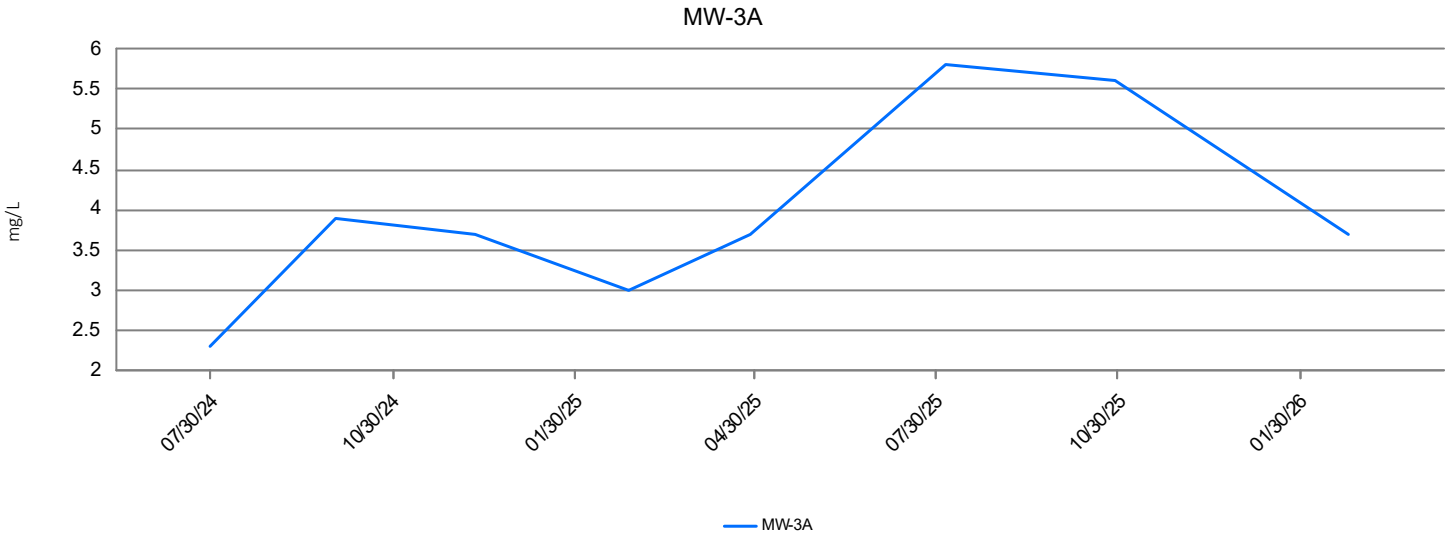
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Organic Carbon (TOC) (mg/L)





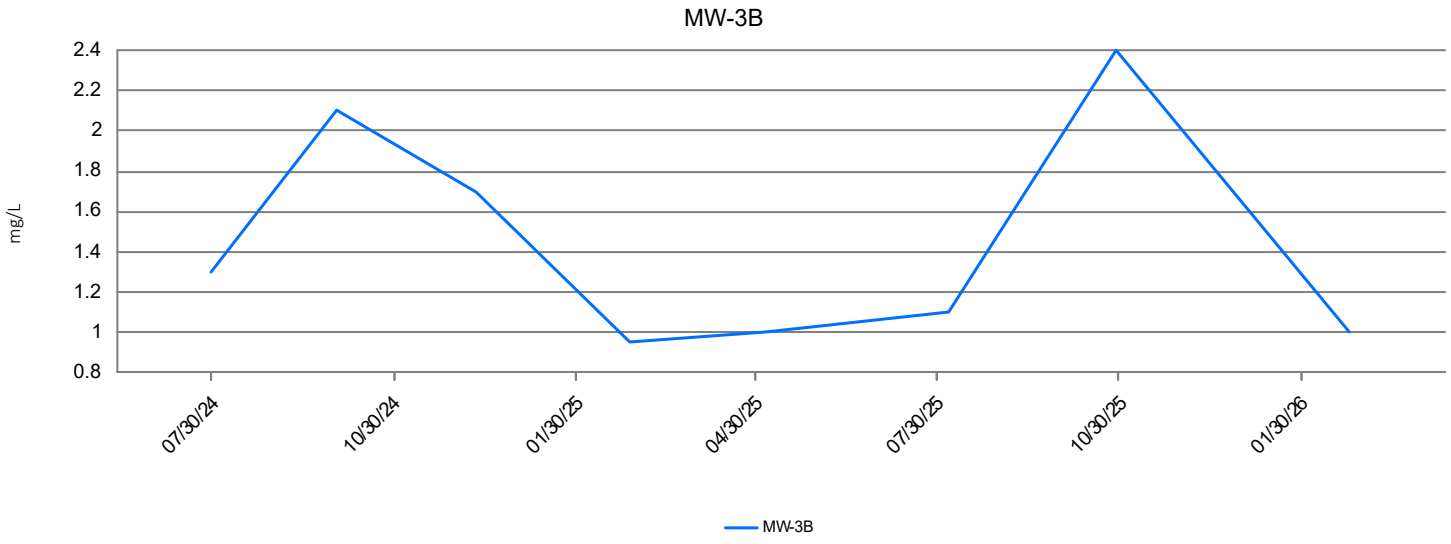


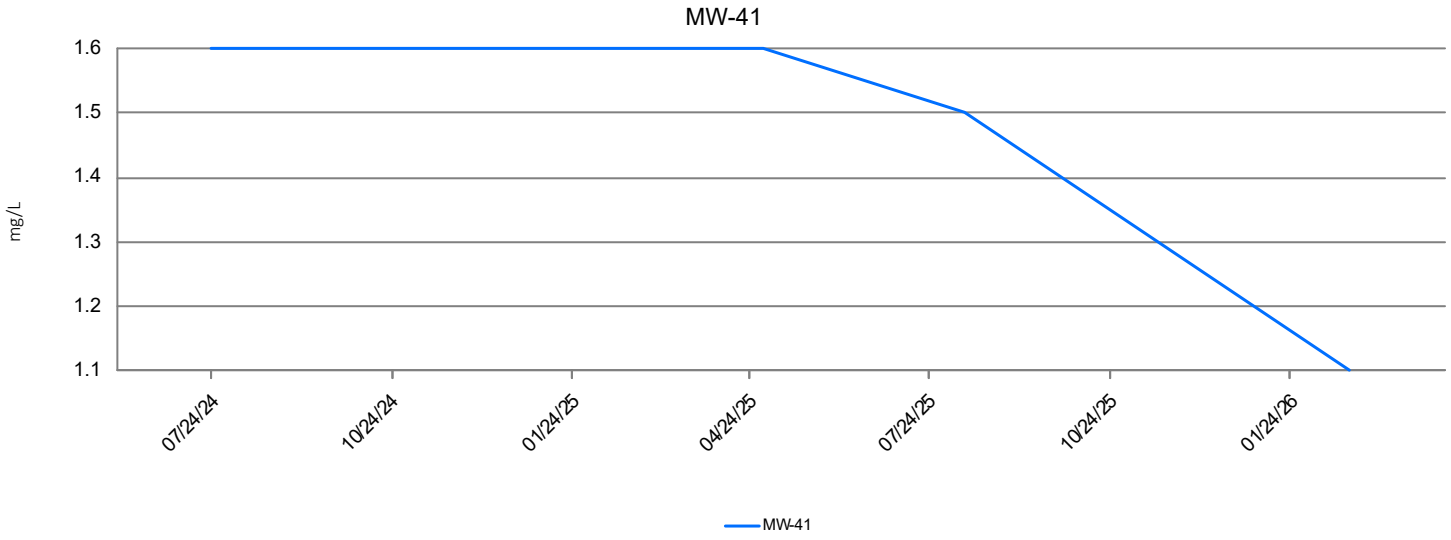
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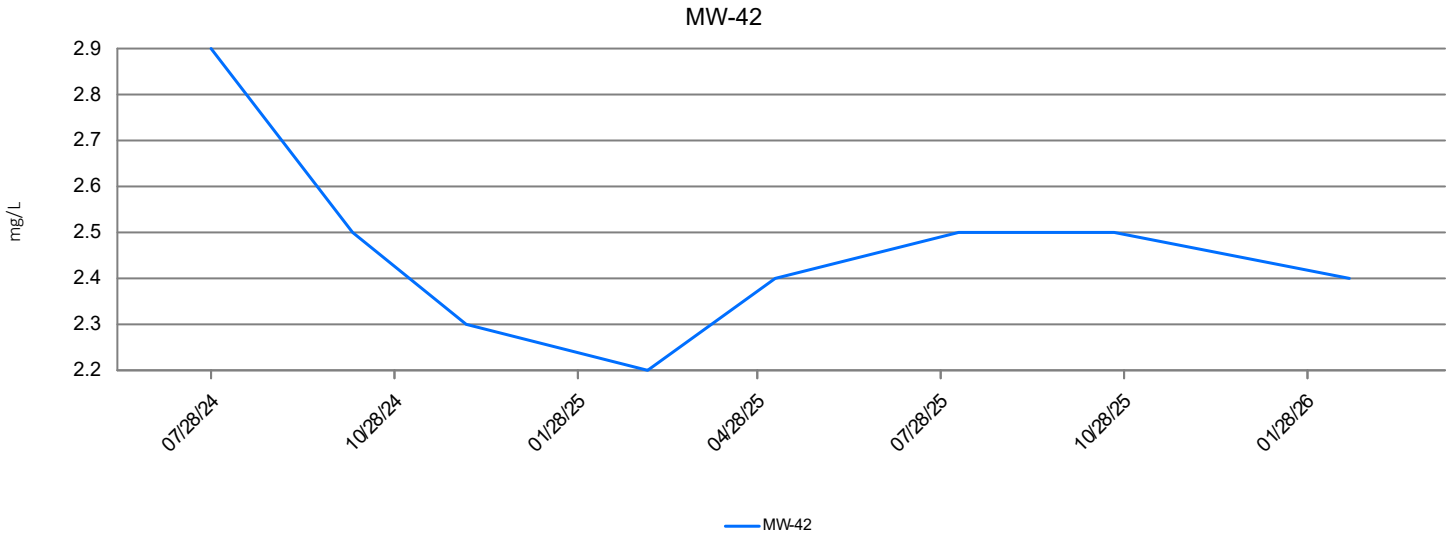
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Organic Carbon (TOC) (mg/L)





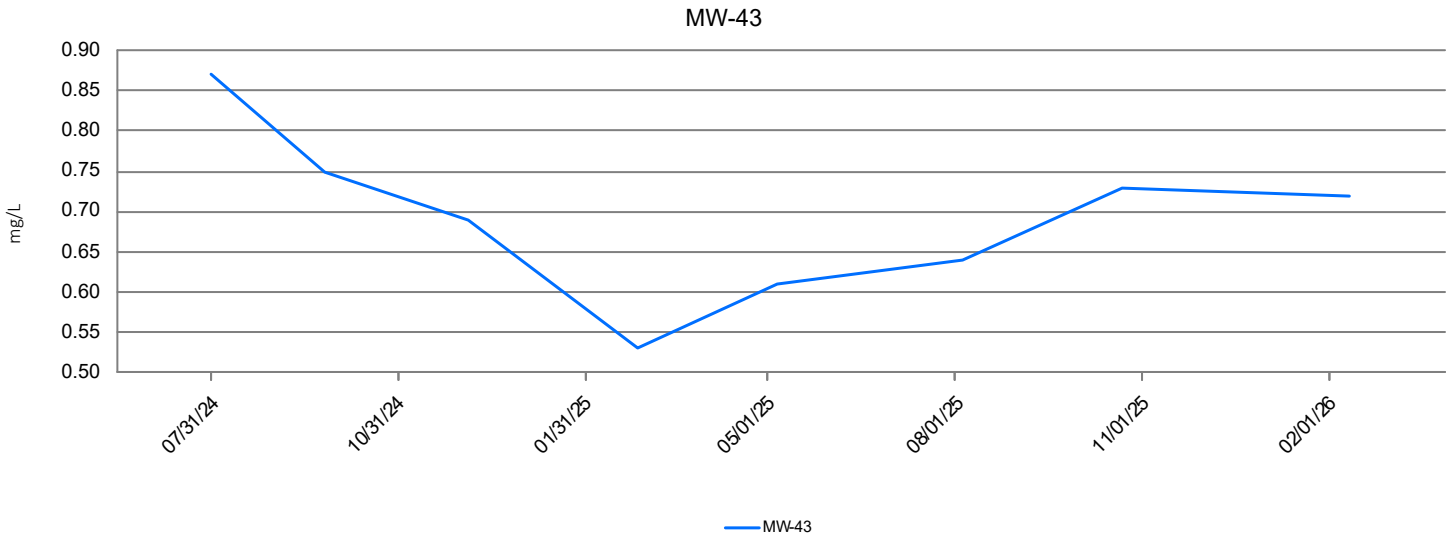


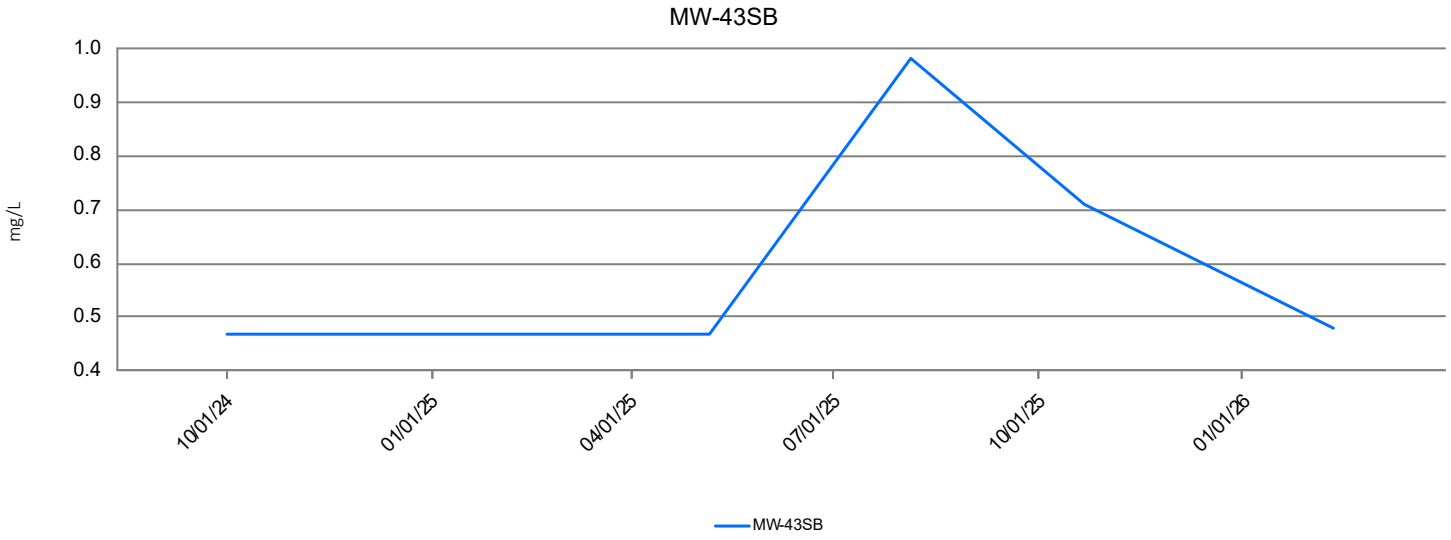
Variable Graphical Report

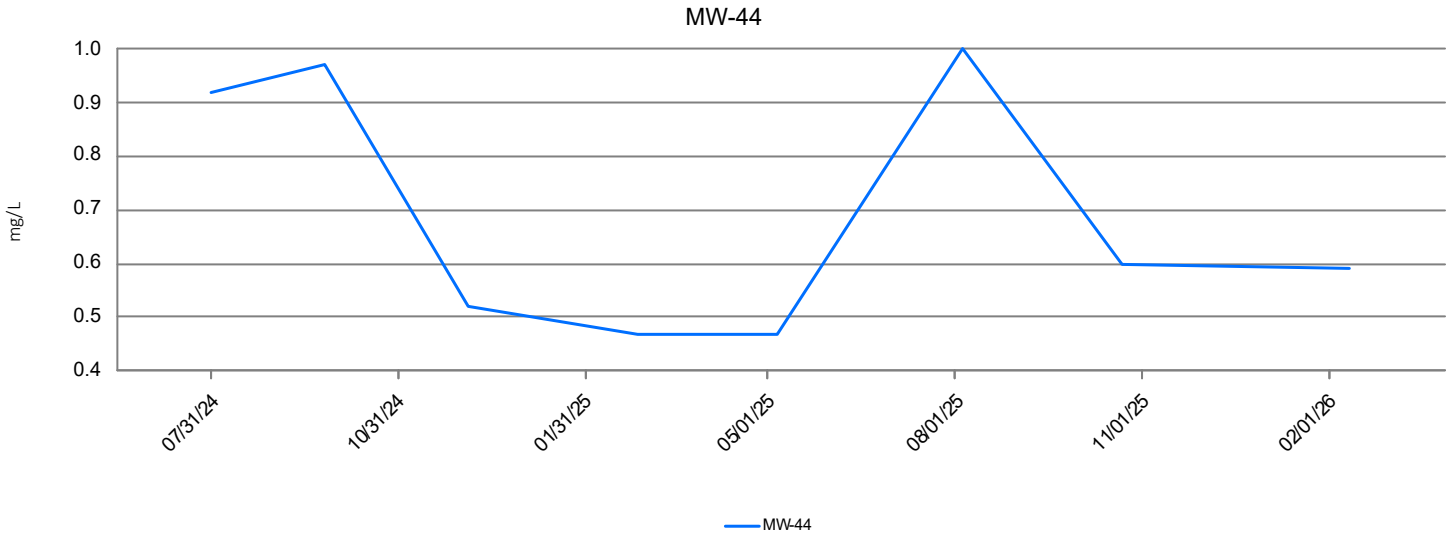
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Organic Carbon (TOC) (mg/L)





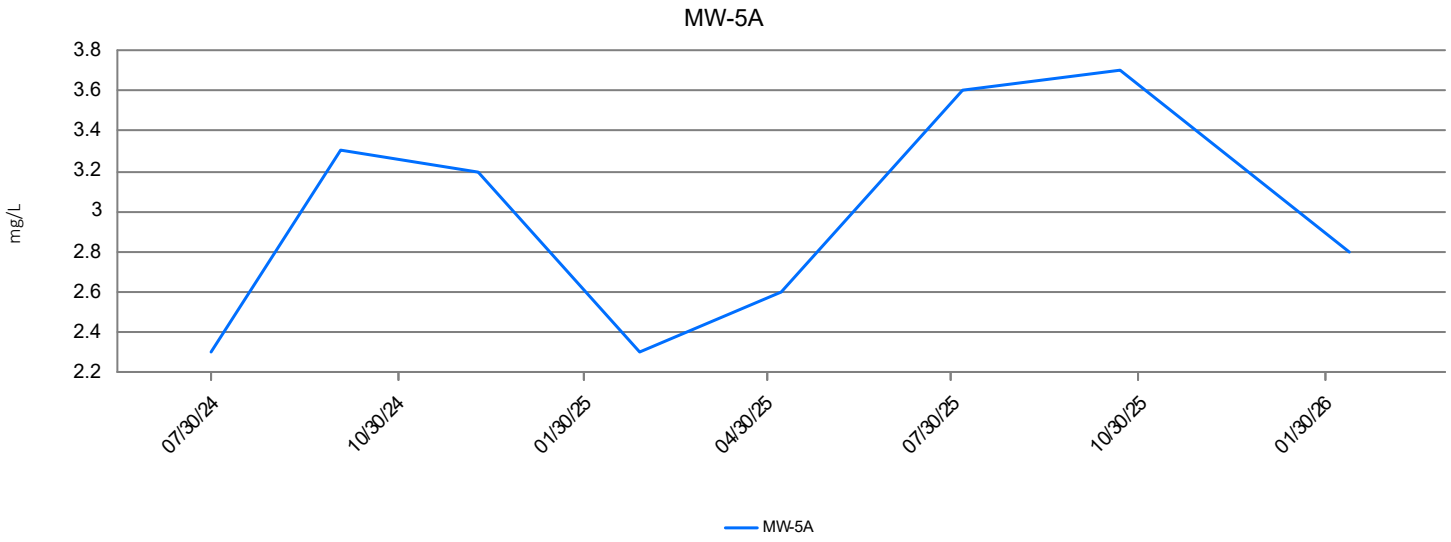


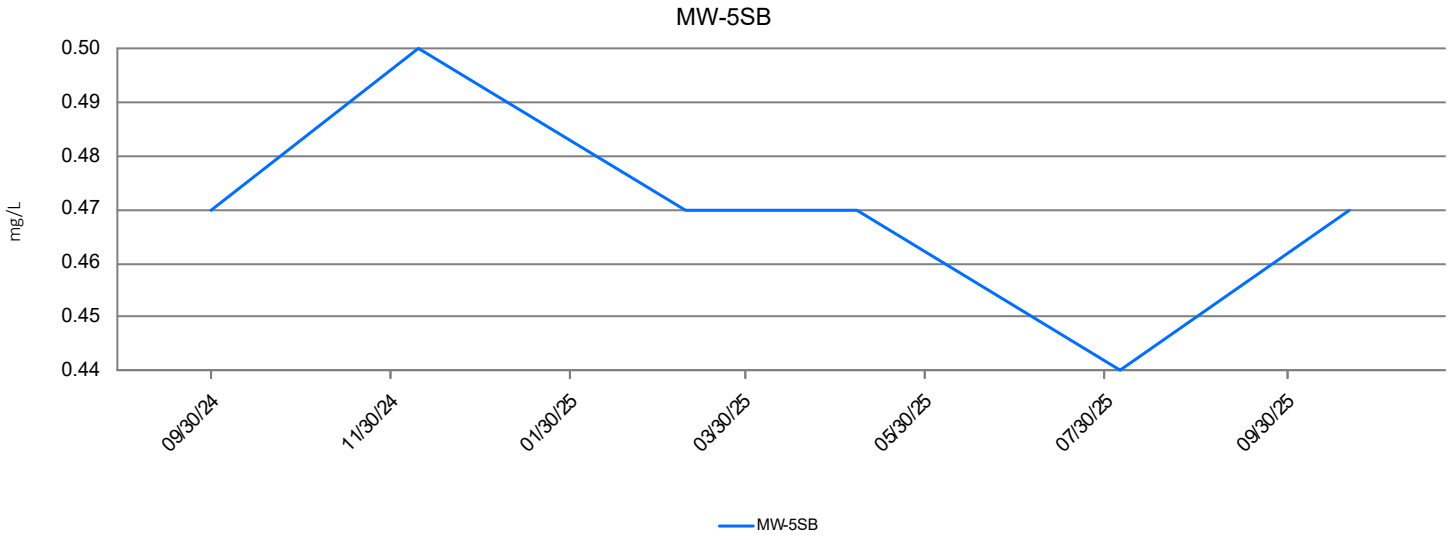
Variable Graphical Report

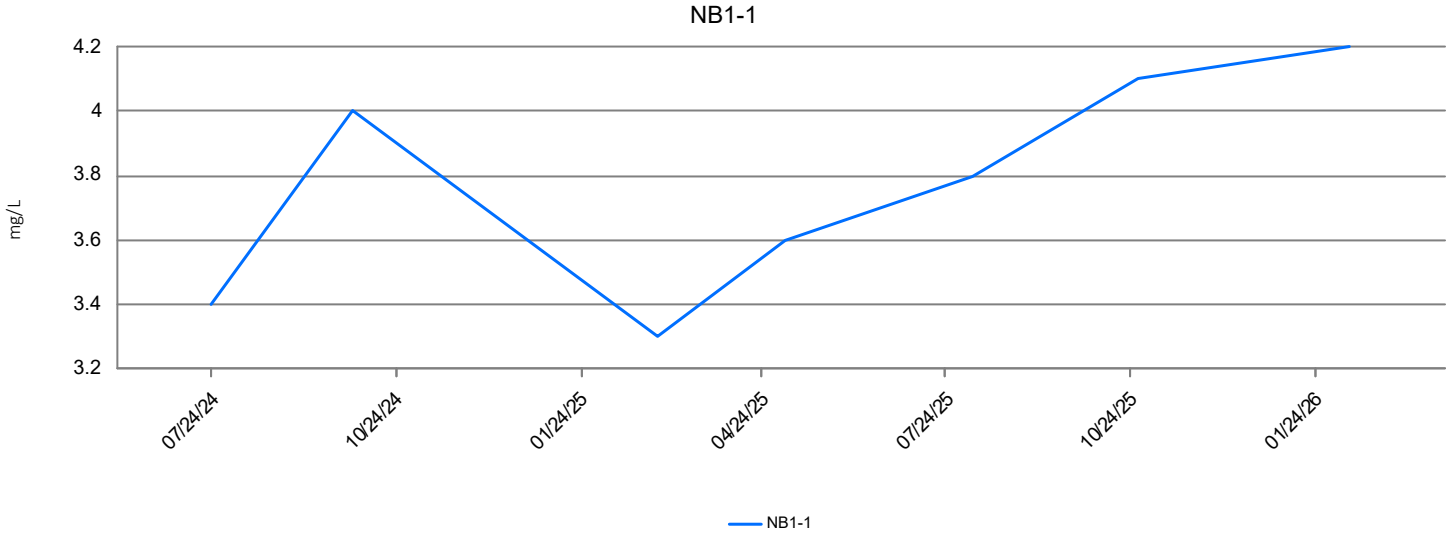
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Organic Carbon (TOC) (mg/L)





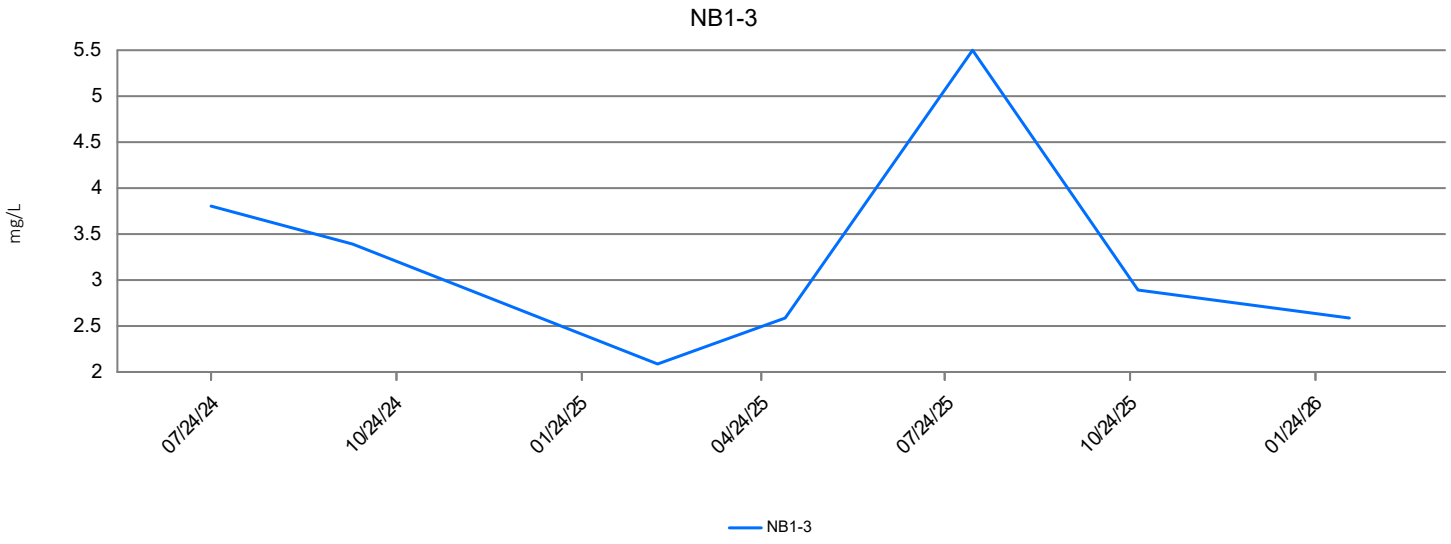


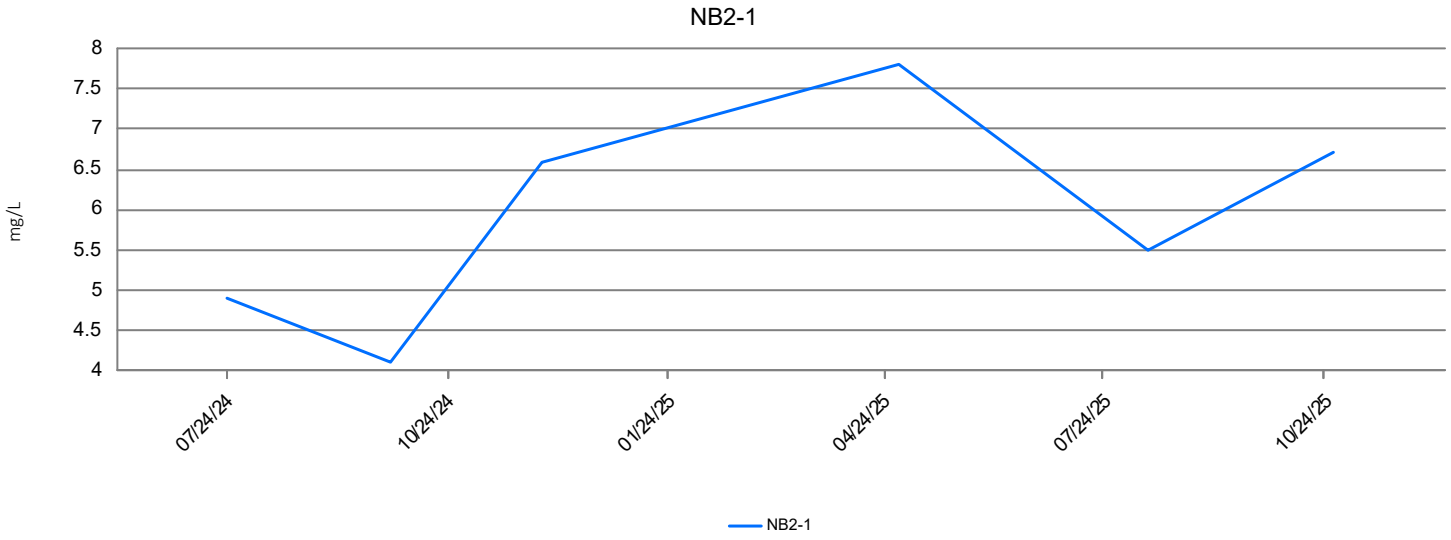
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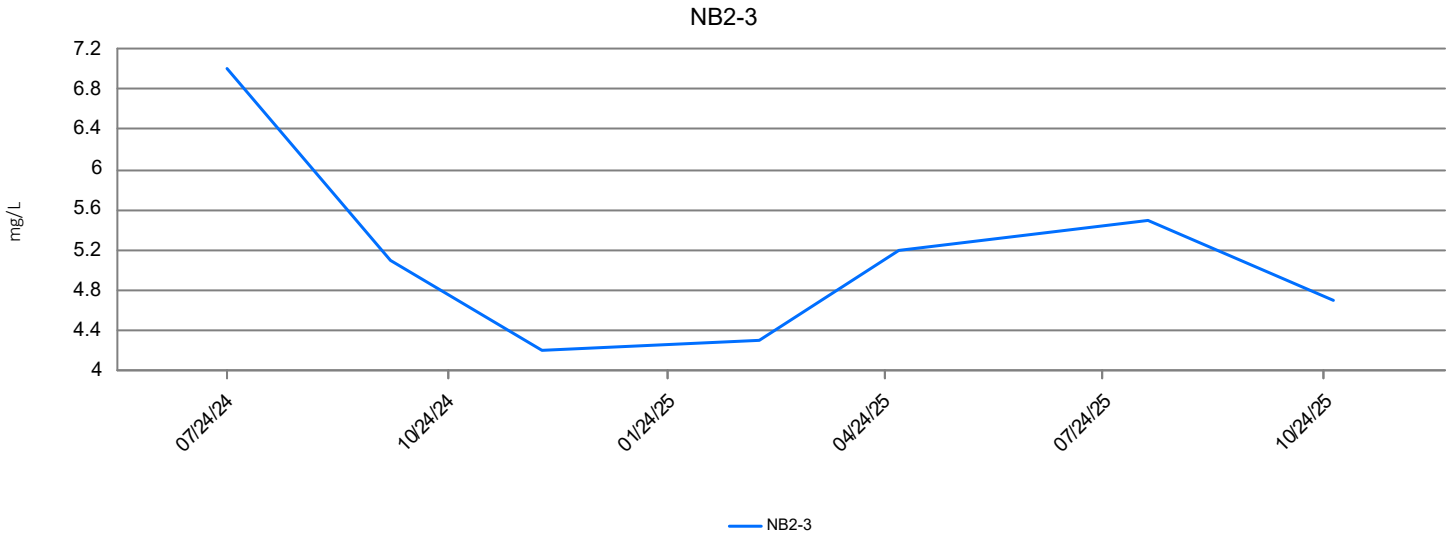
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Organic Carbon (TOC) (mg/L)







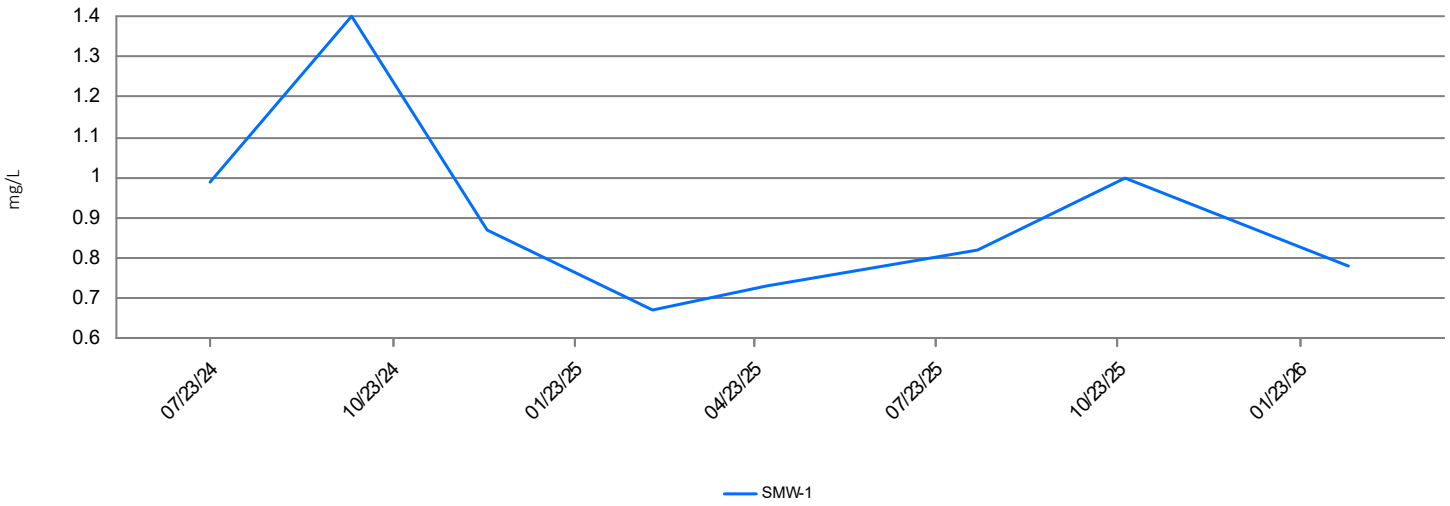
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

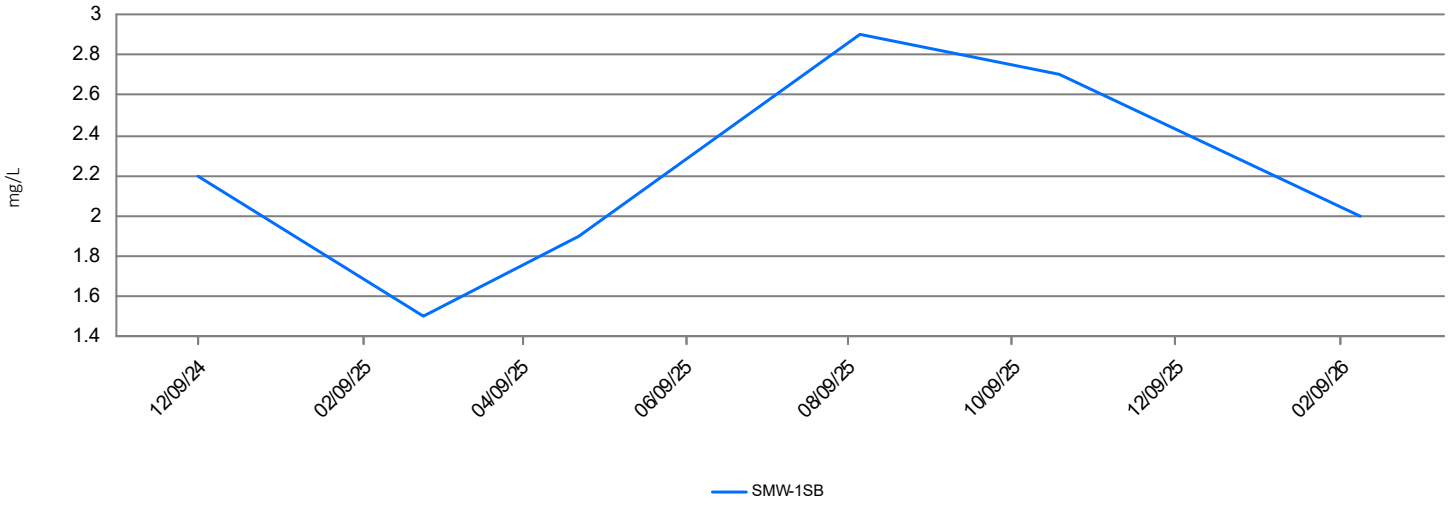
MonitorPro

No Group Selected, Total Organic Carbon (TOC) (mg/L)

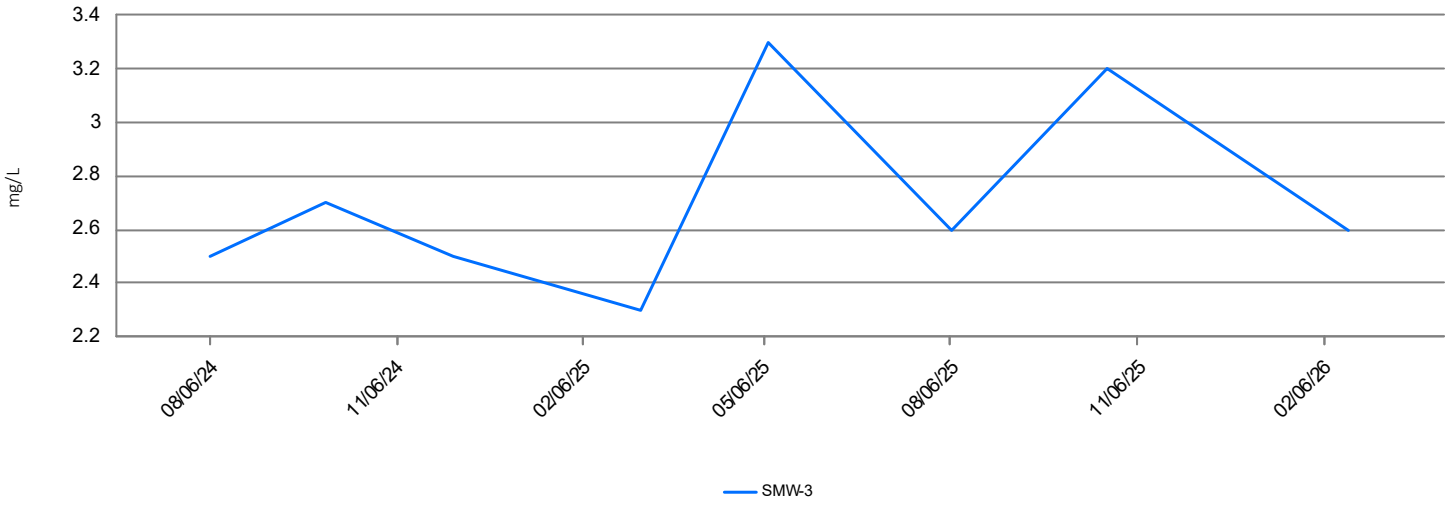
SMW-1



SMW-1SB



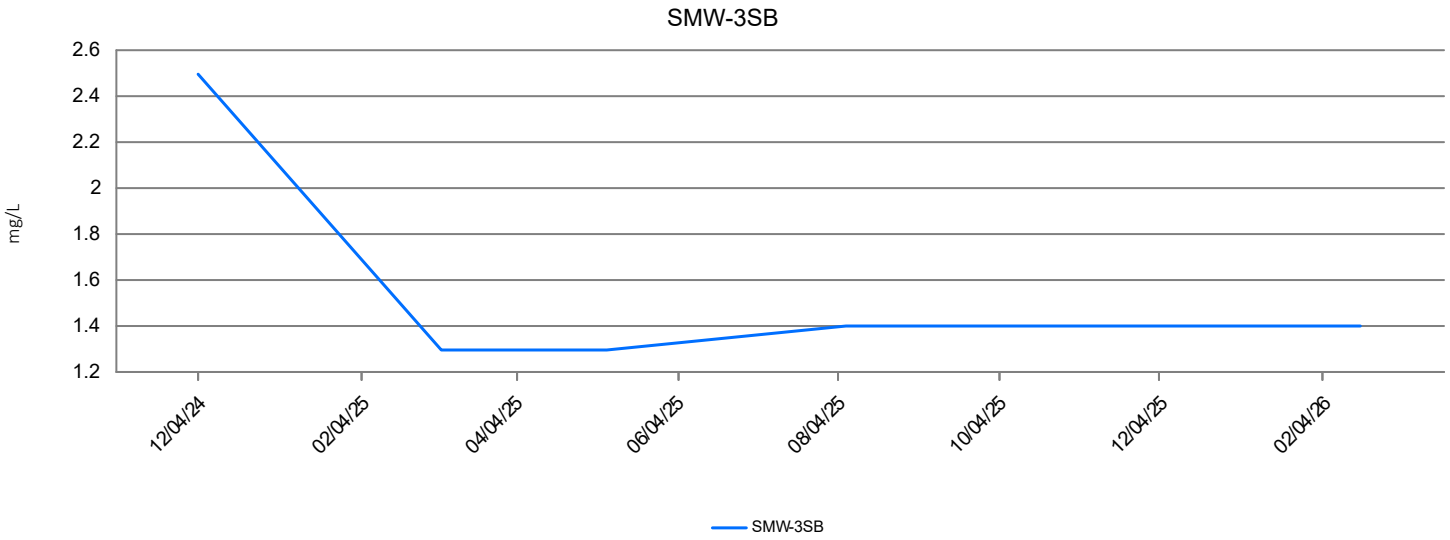
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Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

No Group Selected, Total Organic Carbon (TOC) (mg/L)

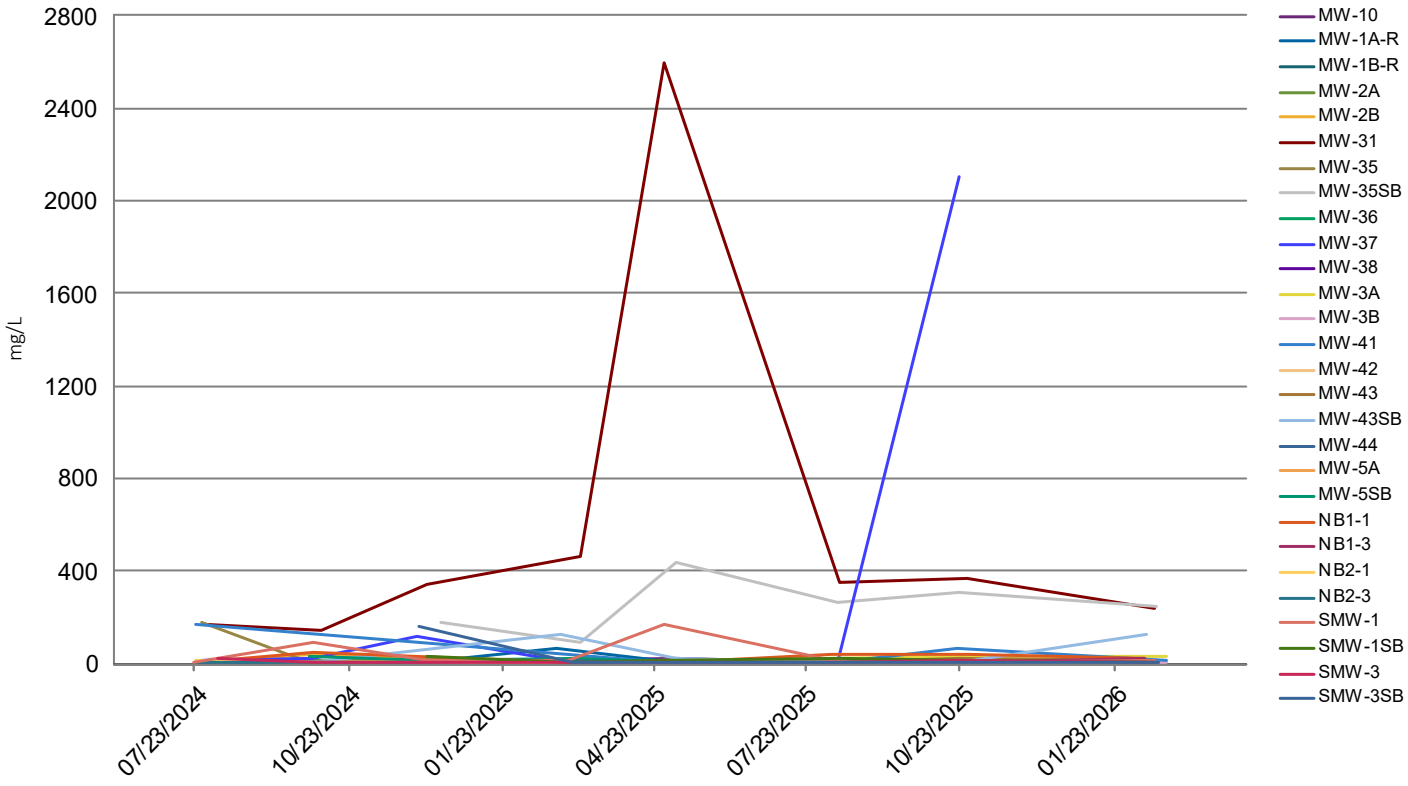


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Suspended Solids (mg/L)

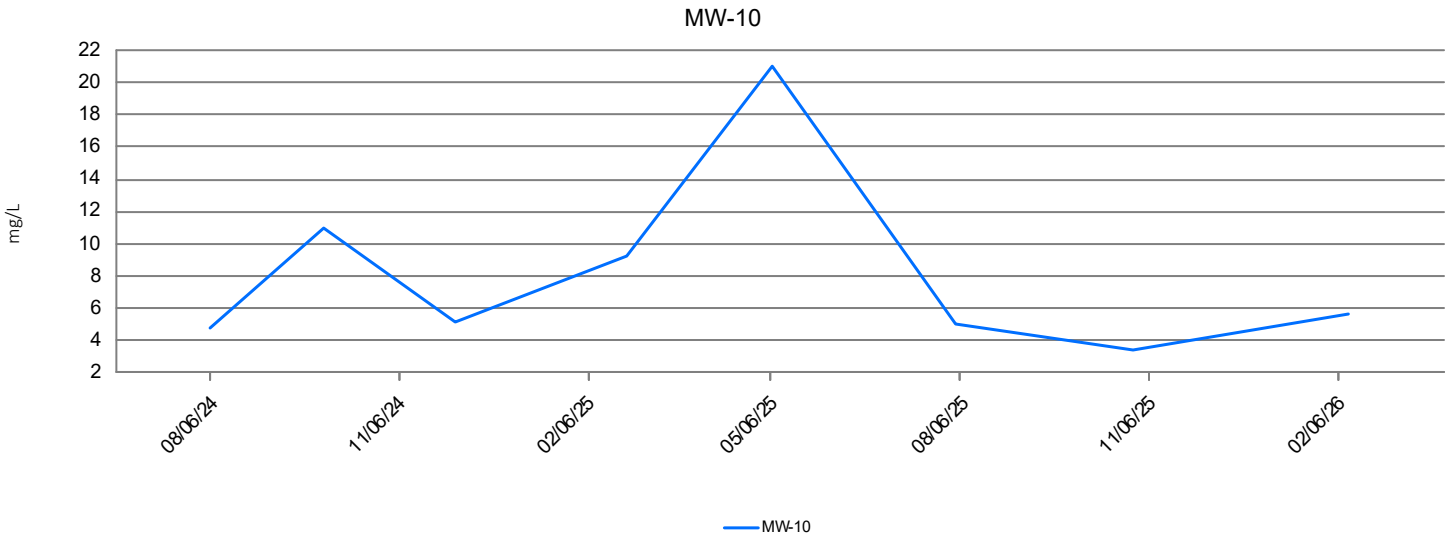


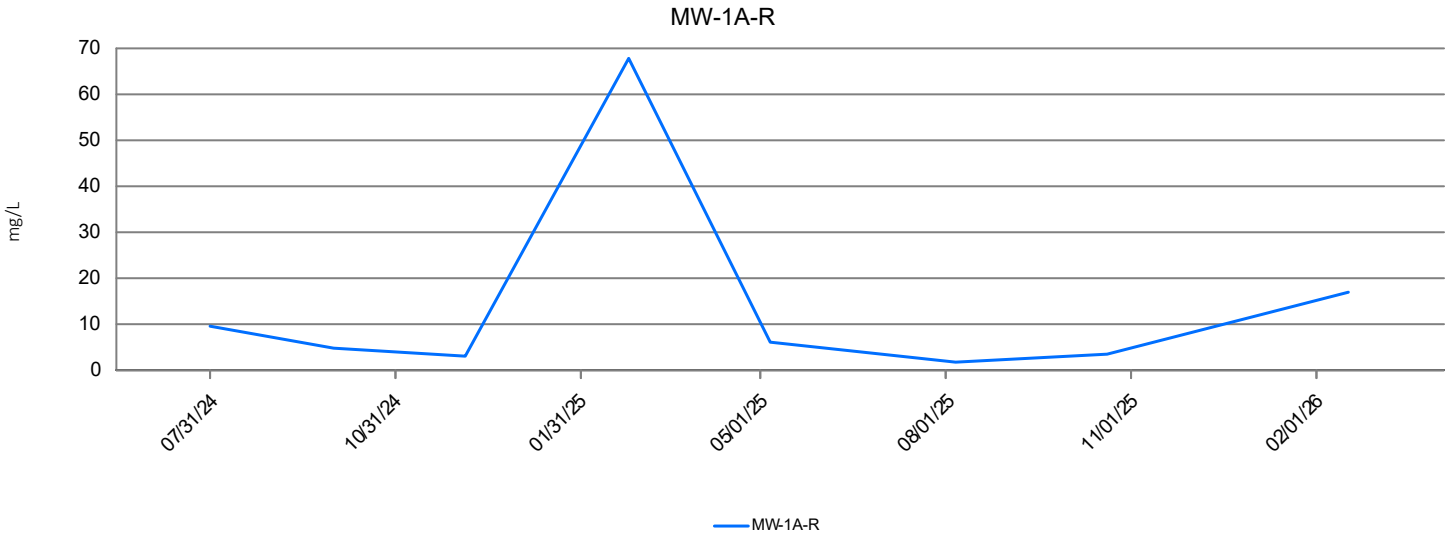
Variable Graphical Report

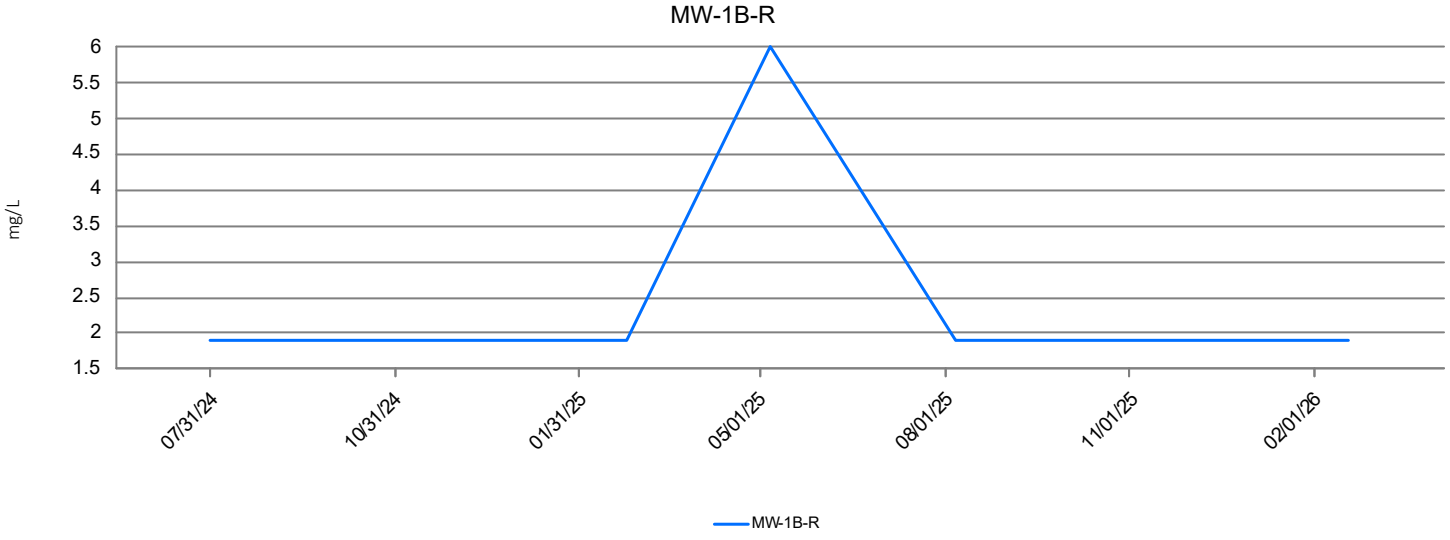
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Suspended Solids (mg/L)





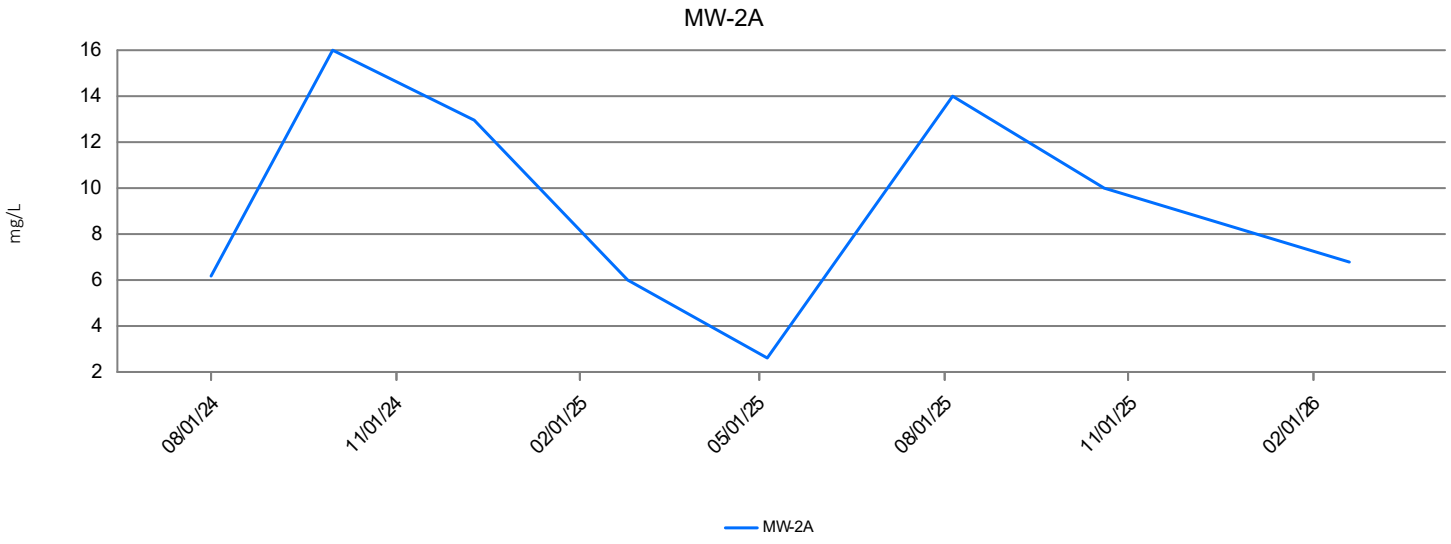


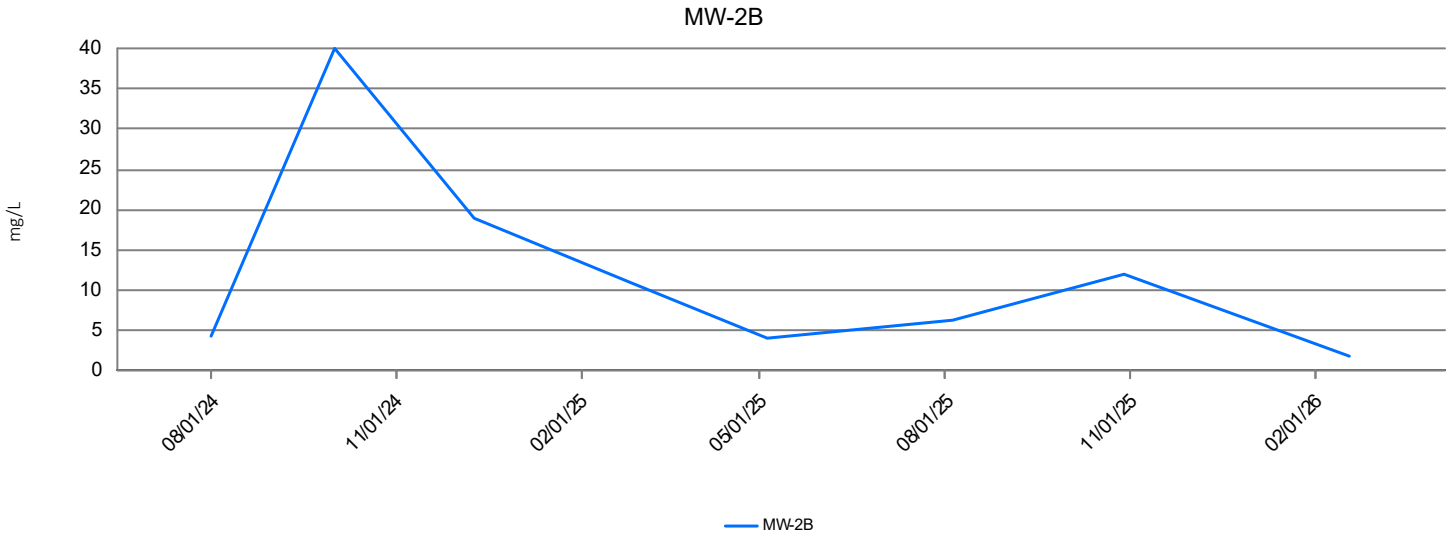
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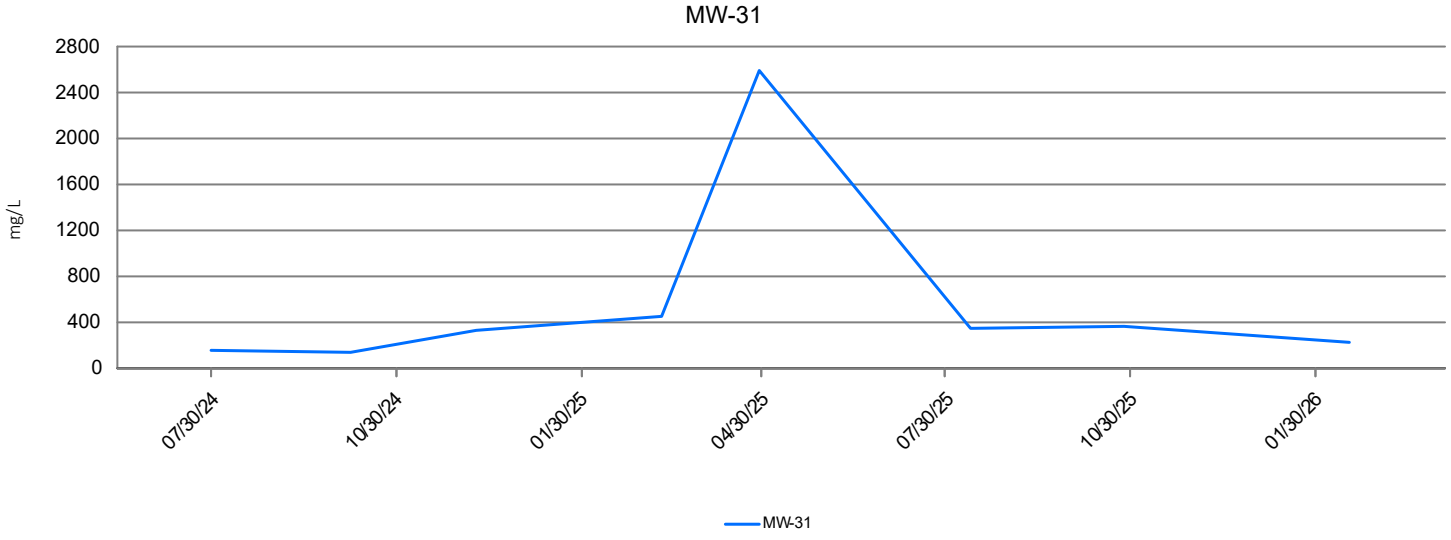
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Suspended Solids (mg/L)





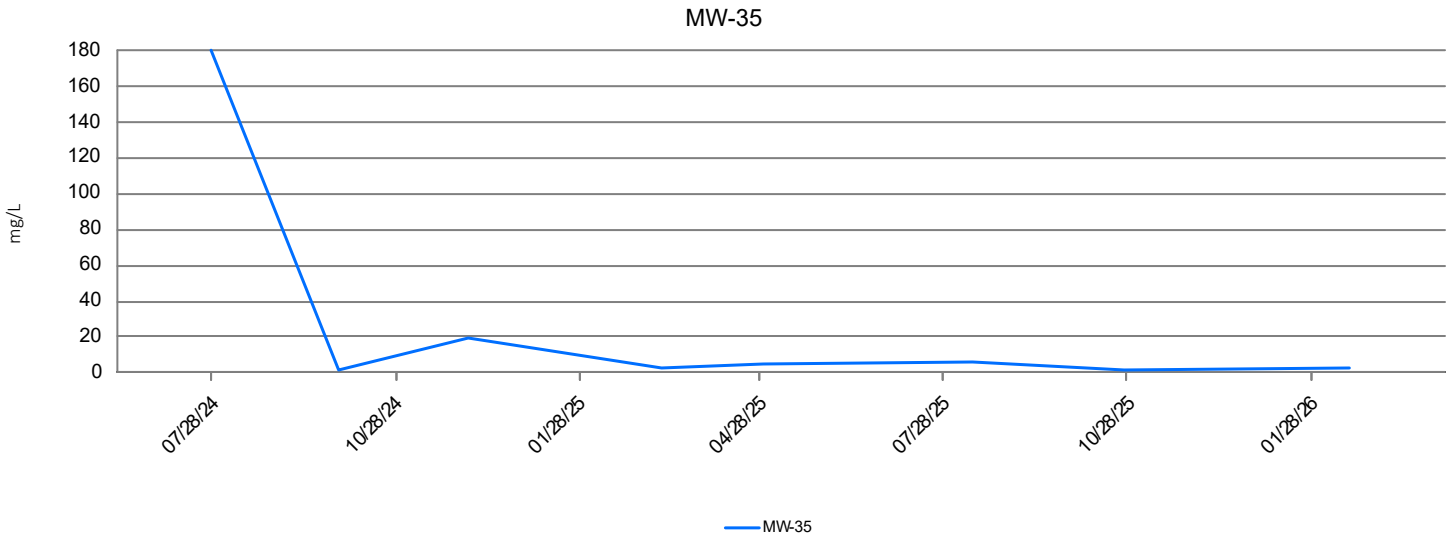


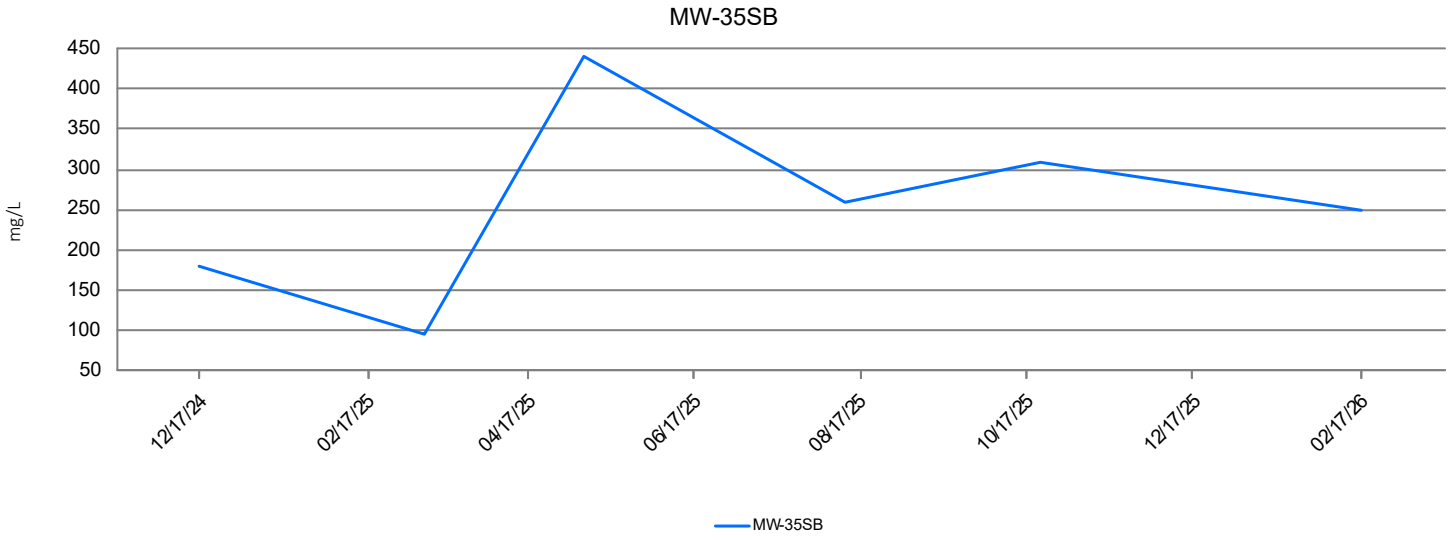
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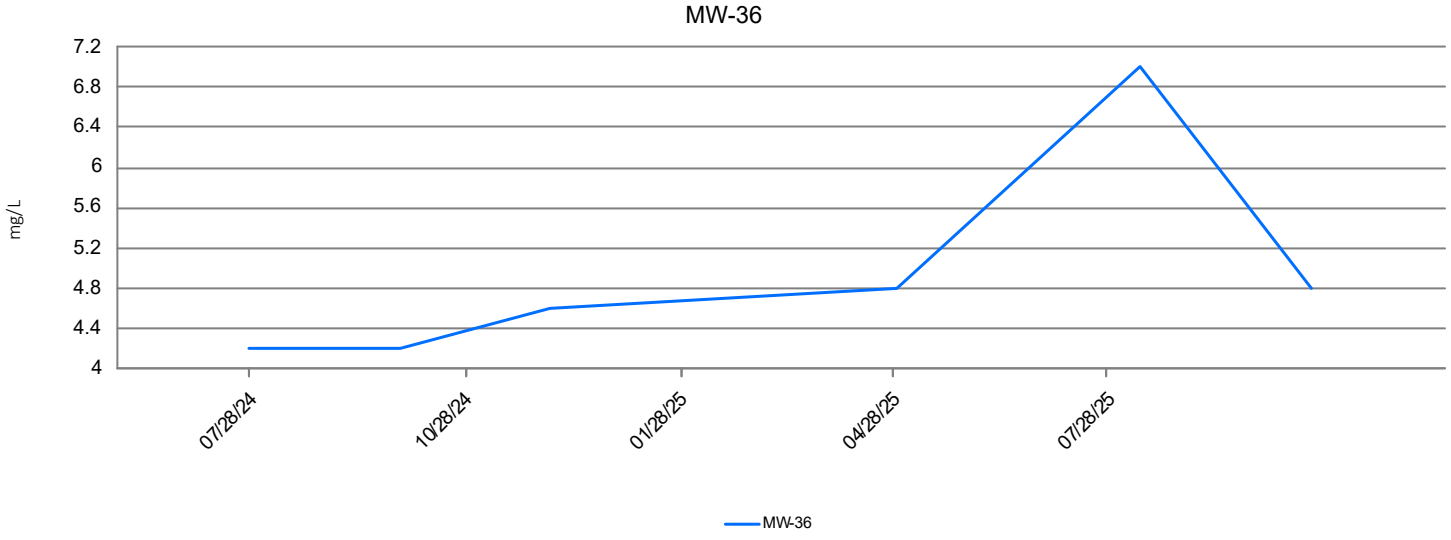
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Suspended Solids (mg/L)





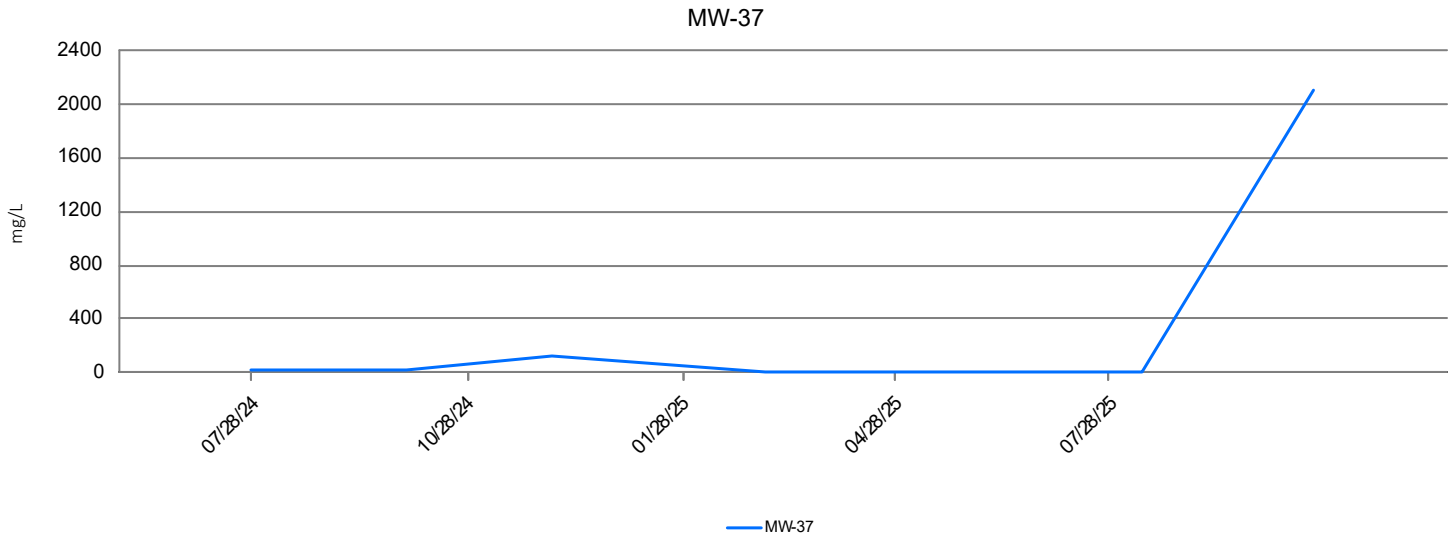


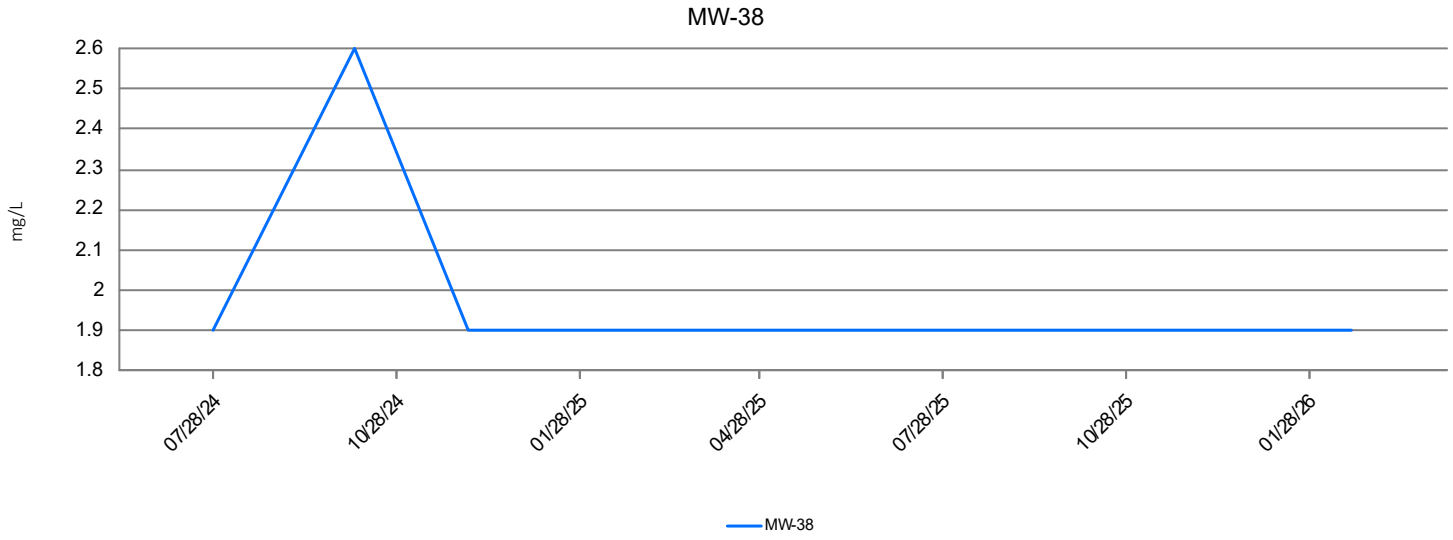
Variable Graphical Report

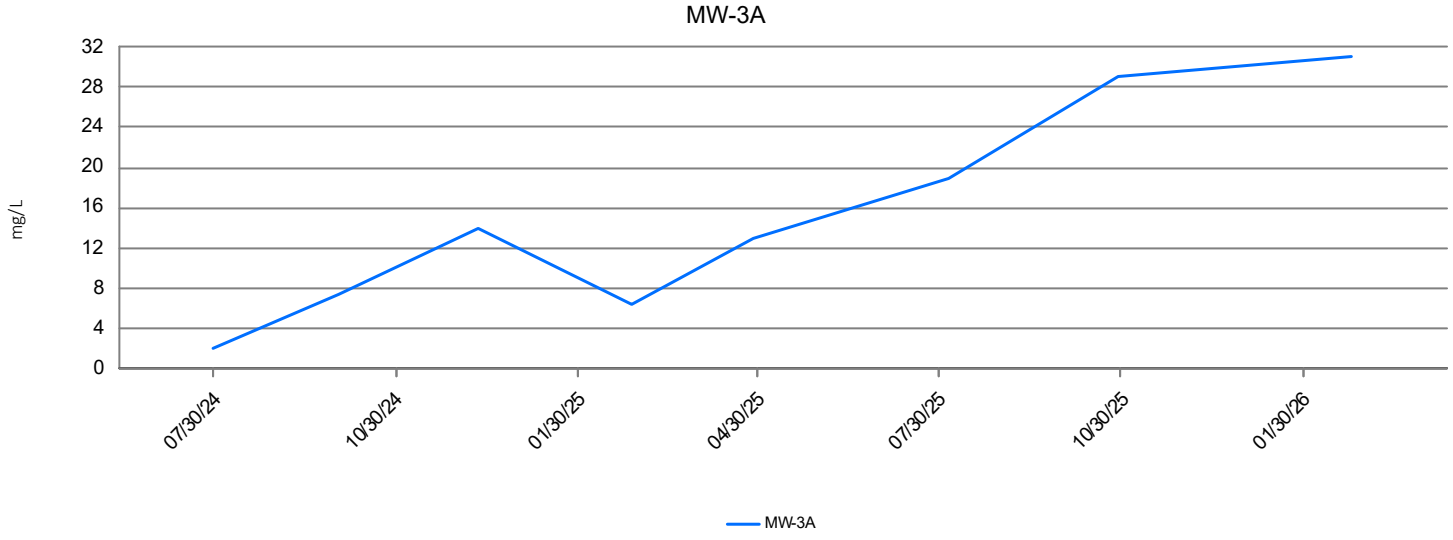
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Suspended Solids (mg/L)







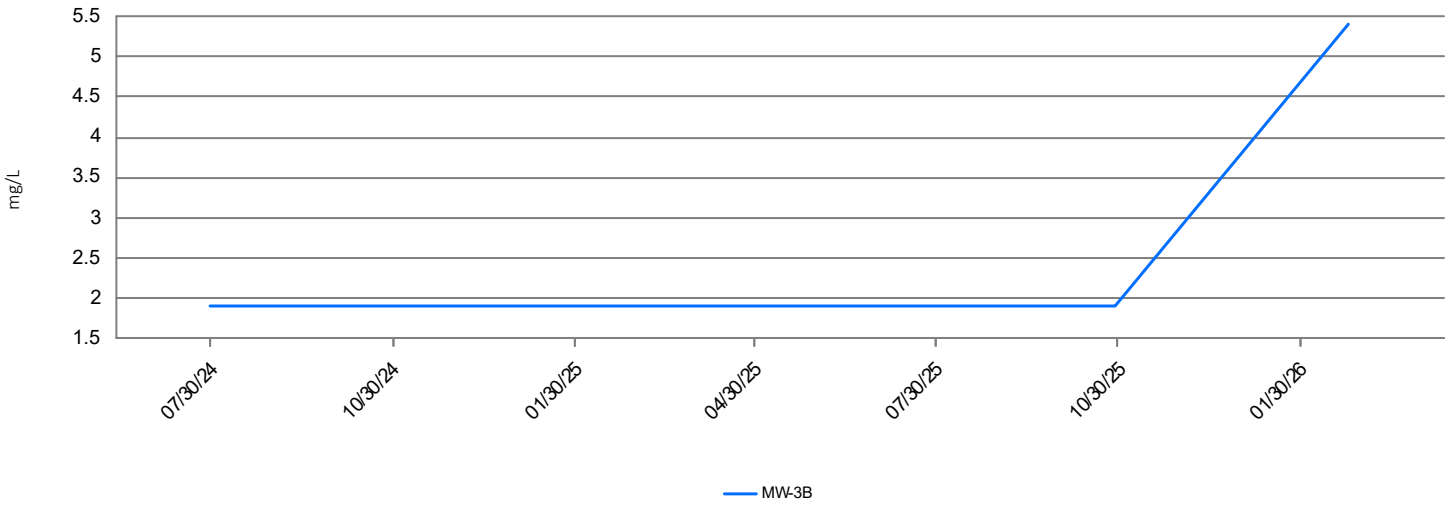
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

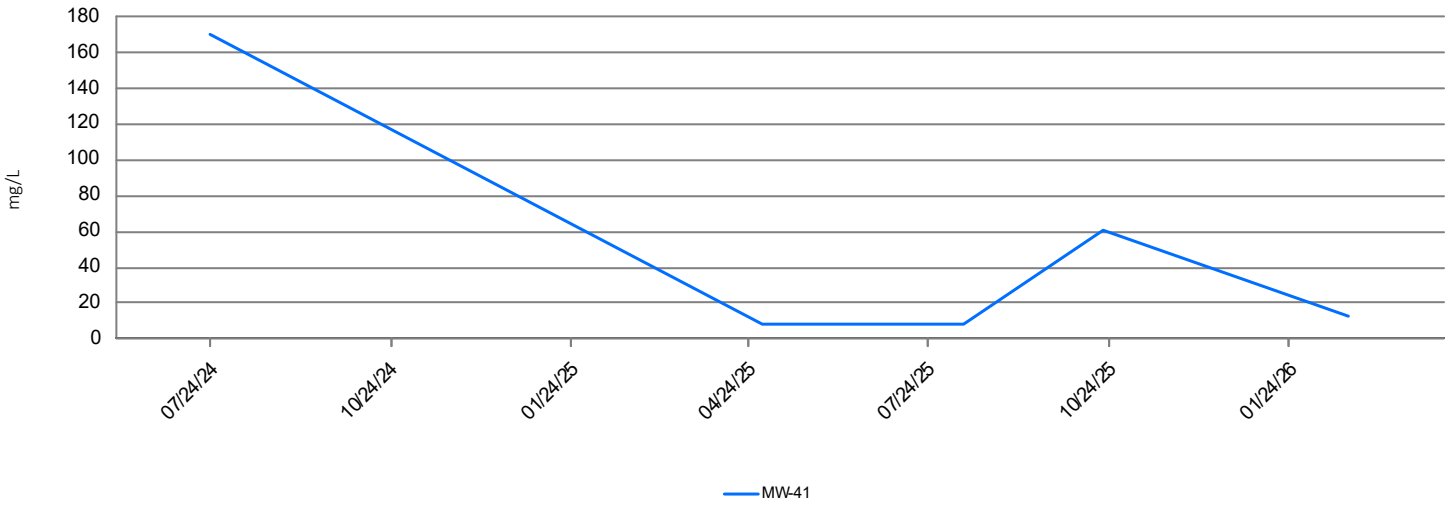
MonitorPro

No Group Selected, Total Suspended Solids (mg/L)

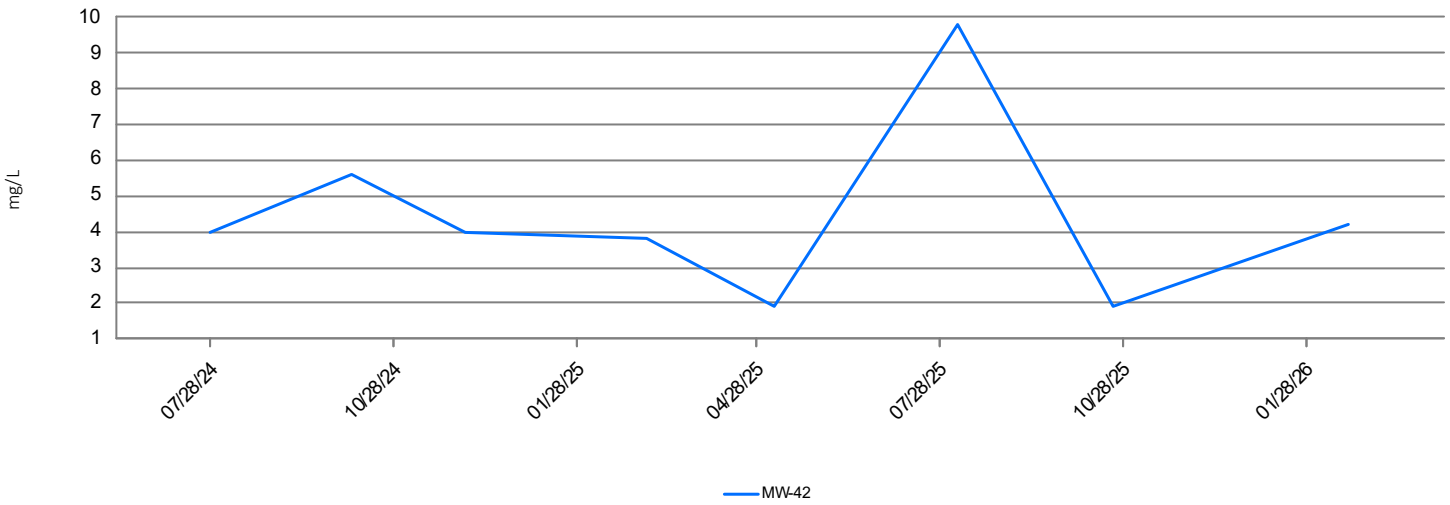
MW-3B



MW-41



MW-42



Printed Date: 05/21/2026

EHS DATA

MCERTS Cert. no. Sira MC090140/02

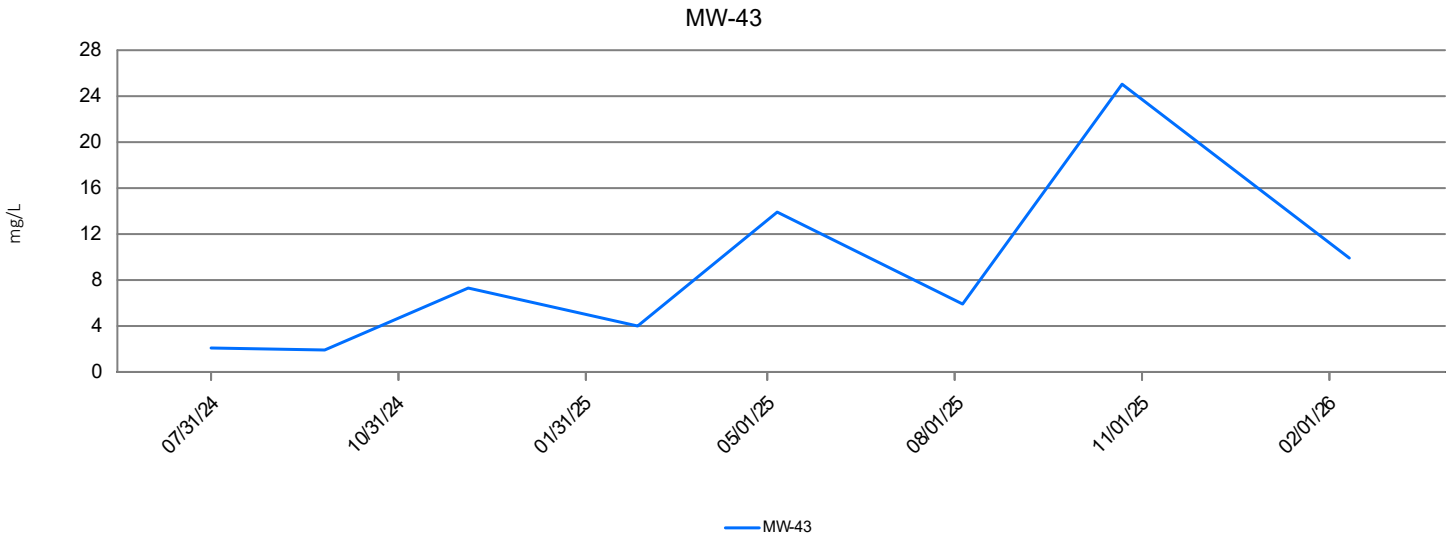
MCERTS

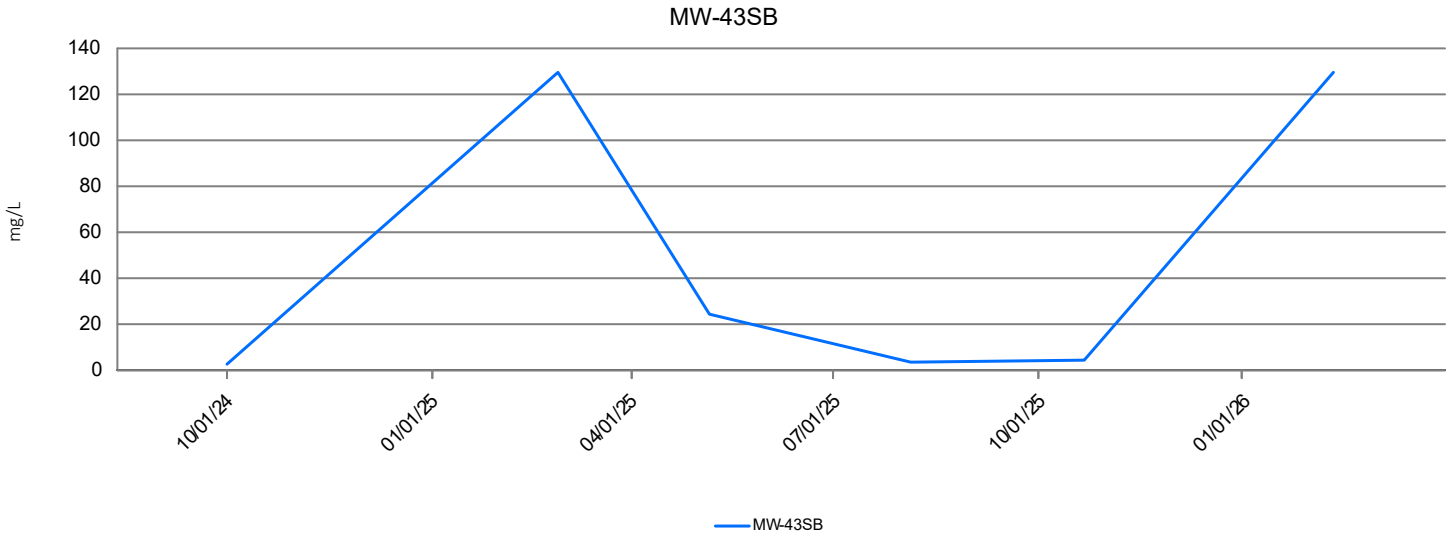
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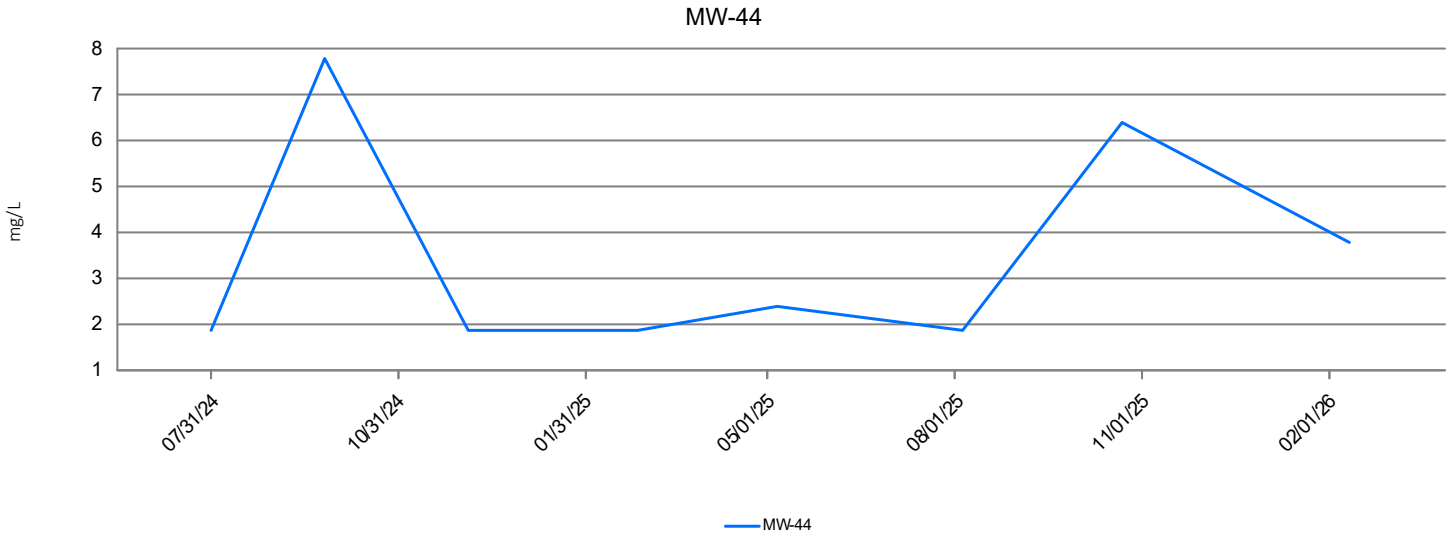
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Suspended Solids (mg/L)







Printed Date: 05/21/2026

EHS DATA

MCERTS Cert. no. Sira MC090140/02

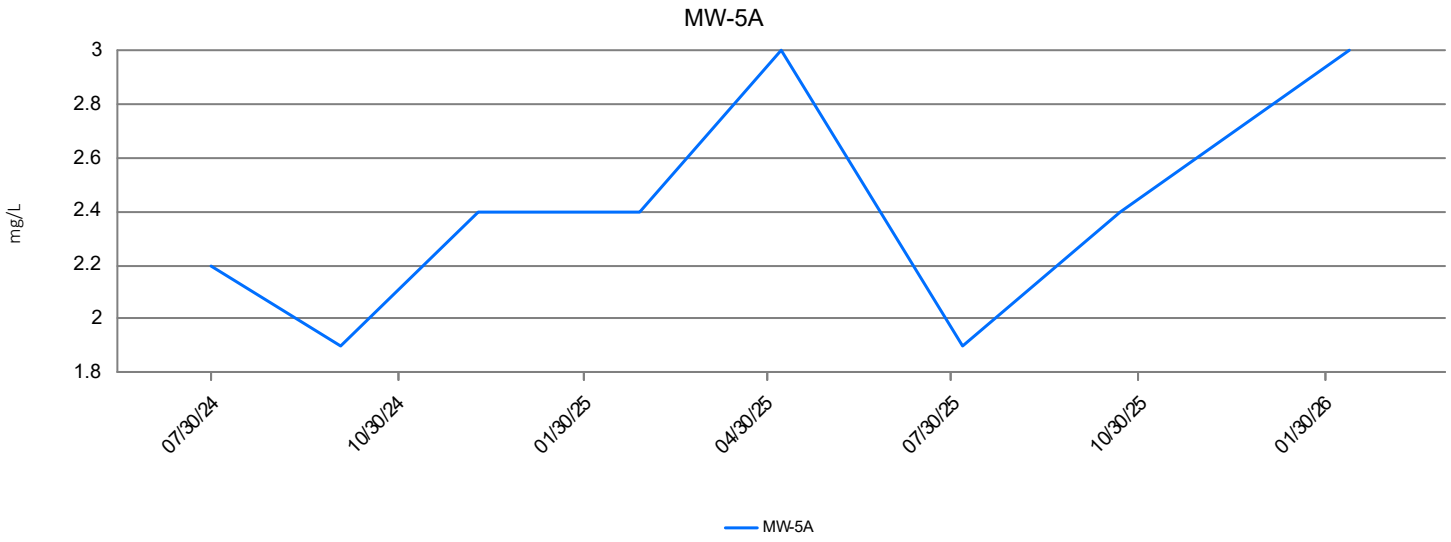
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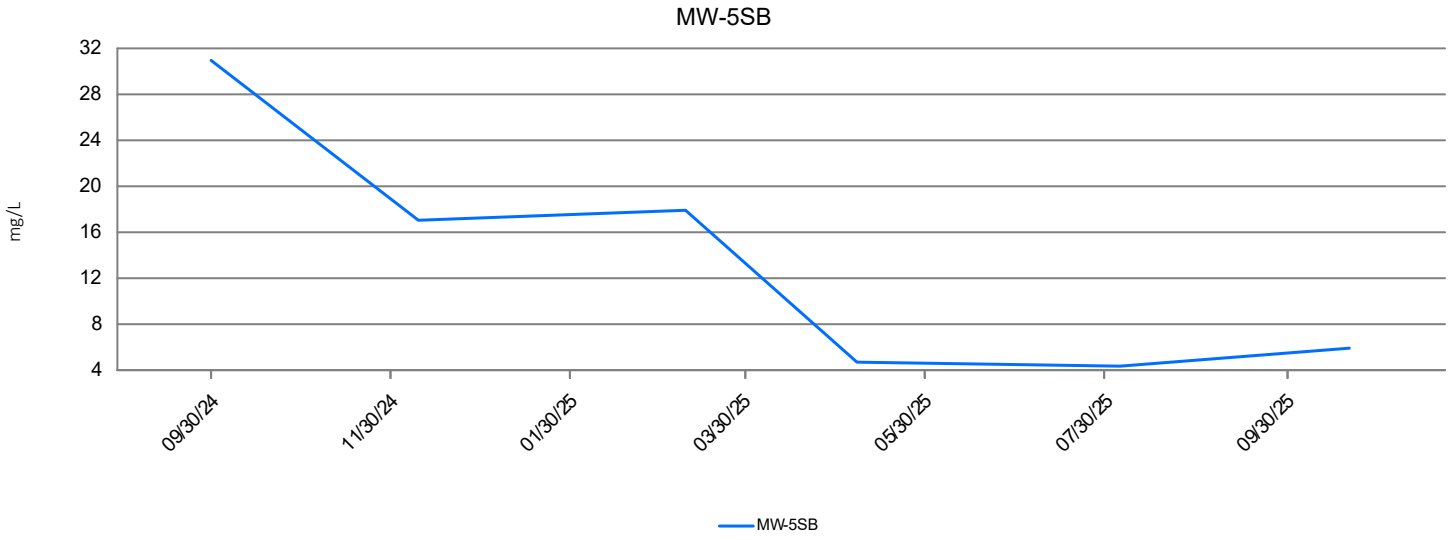
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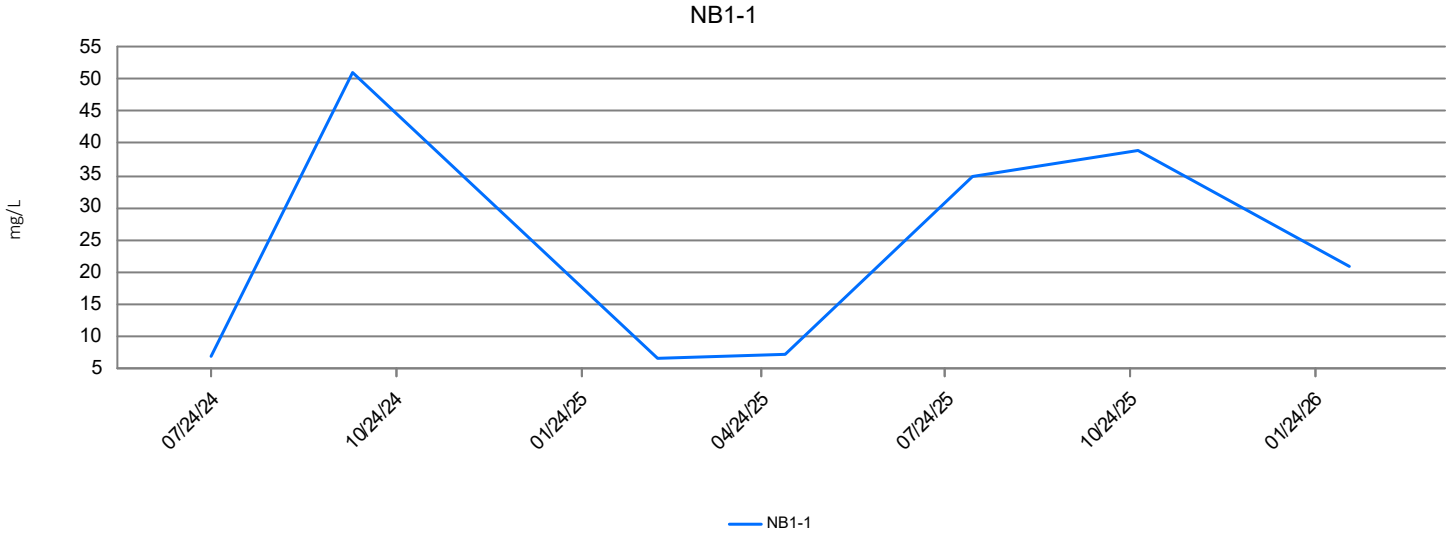
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Suspended Solids (mg/L)





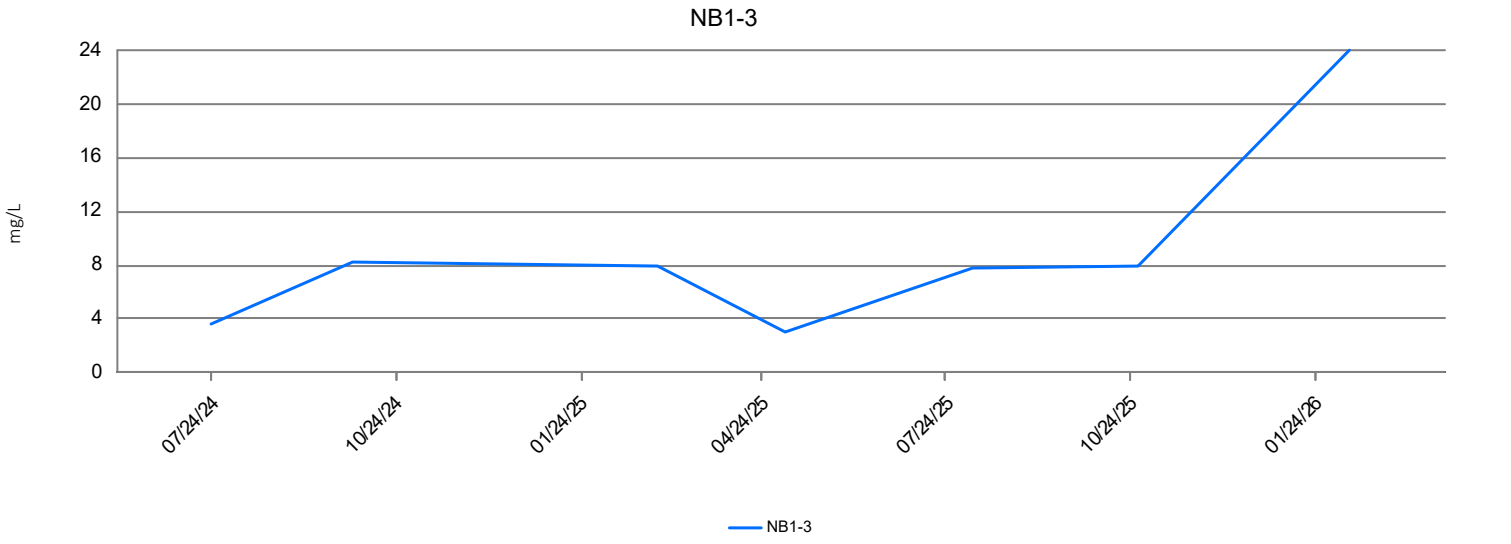


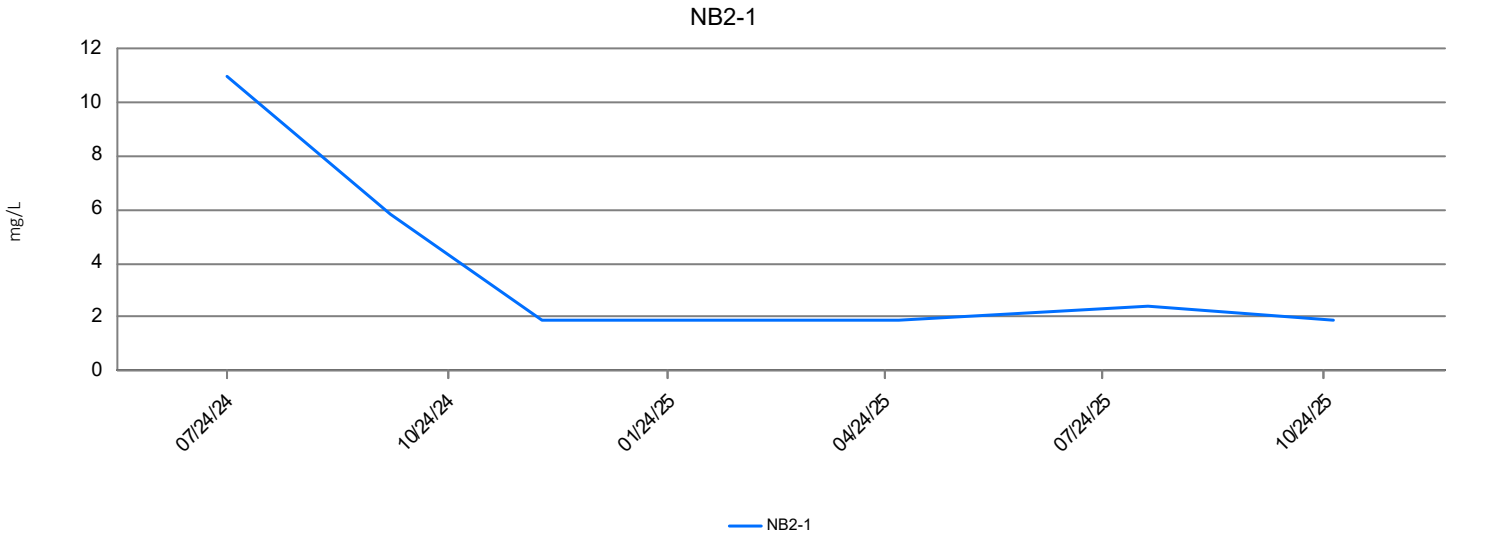
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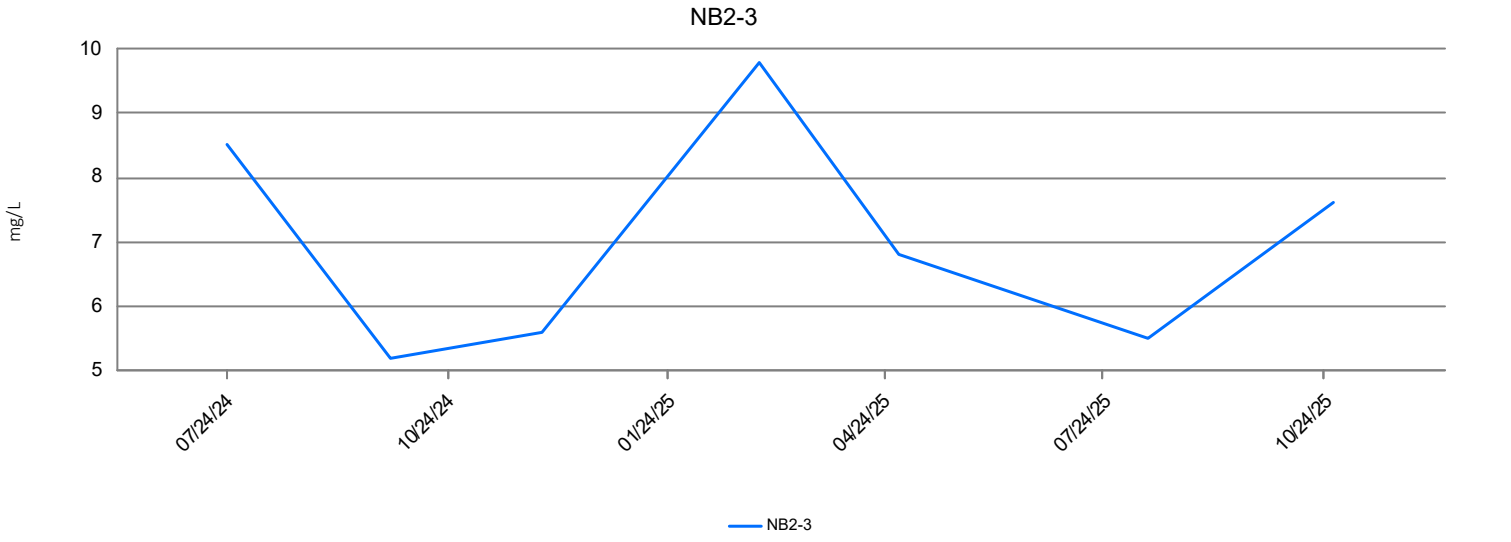
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Suspended Solids (mg/L)







Printed Date: 05/21/2026

EHS DATA

MCERTS Cert. no. Sira MC090140/02

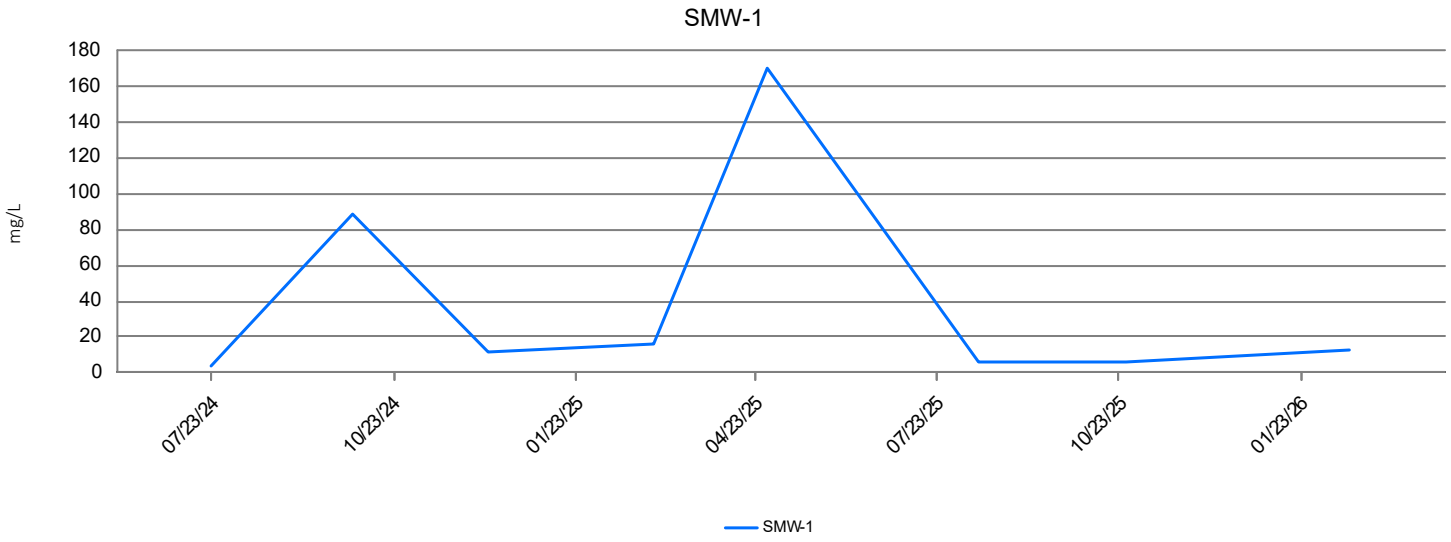
MCERTS

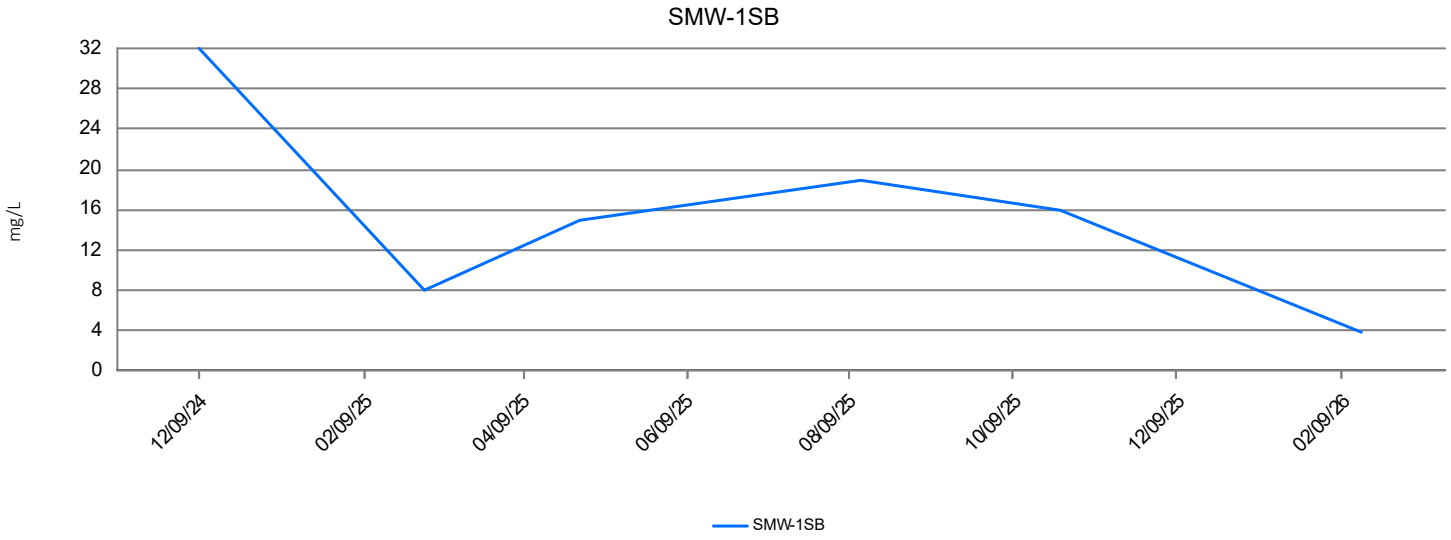
Variable Graphical Report

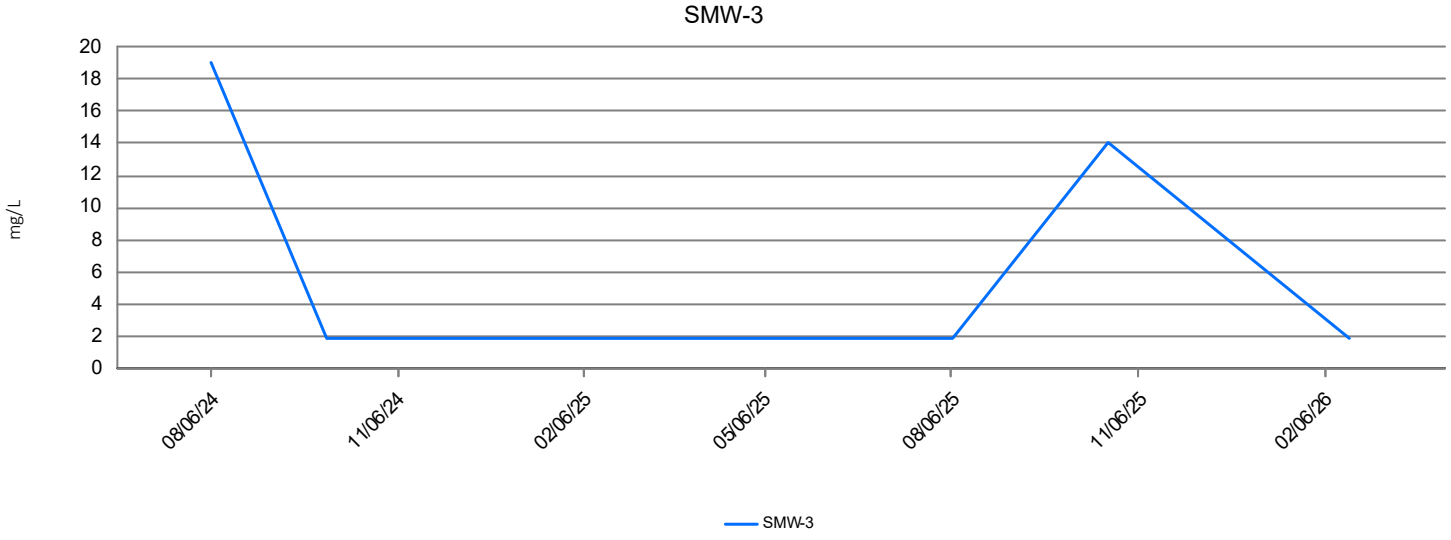
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Suspended Solids (mg/L)





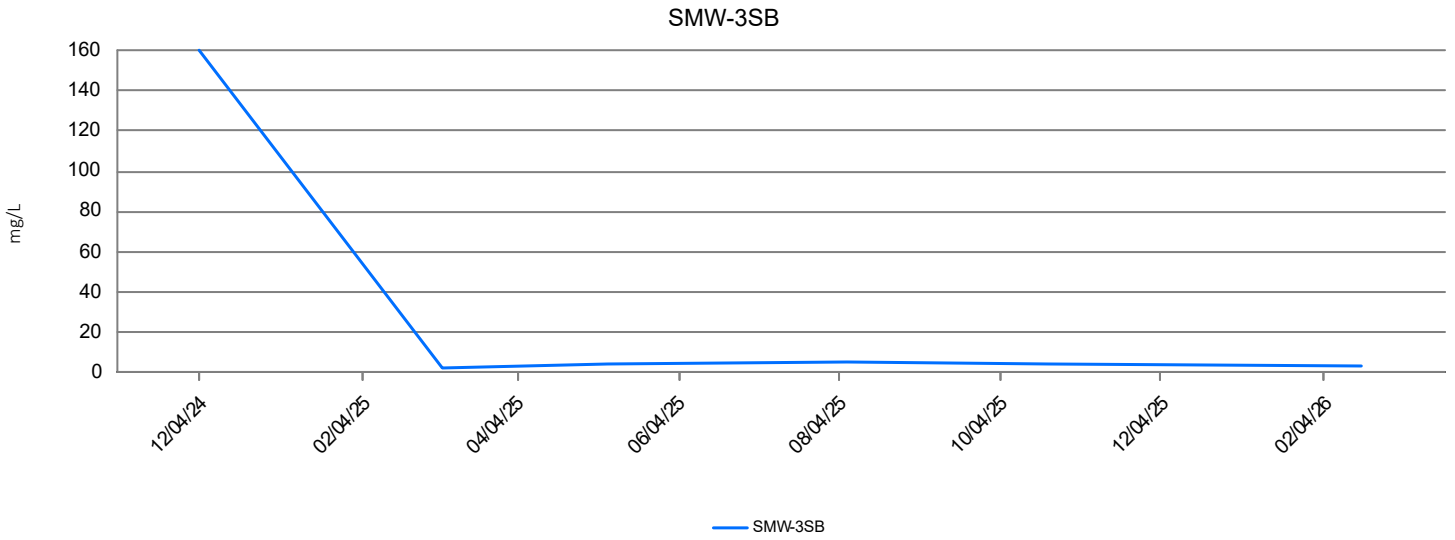


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Total Suspended Solids (mg/L)

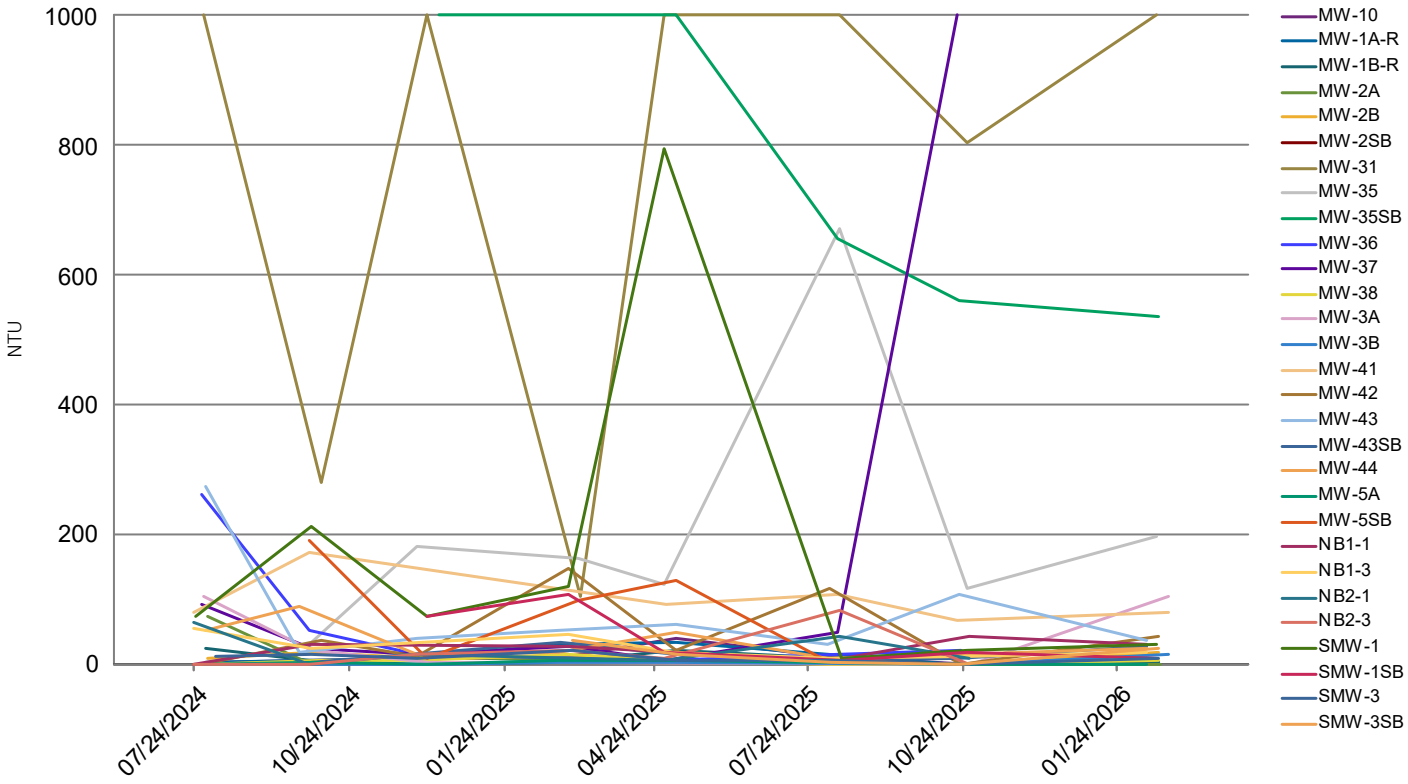


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Turbidity (NTU)



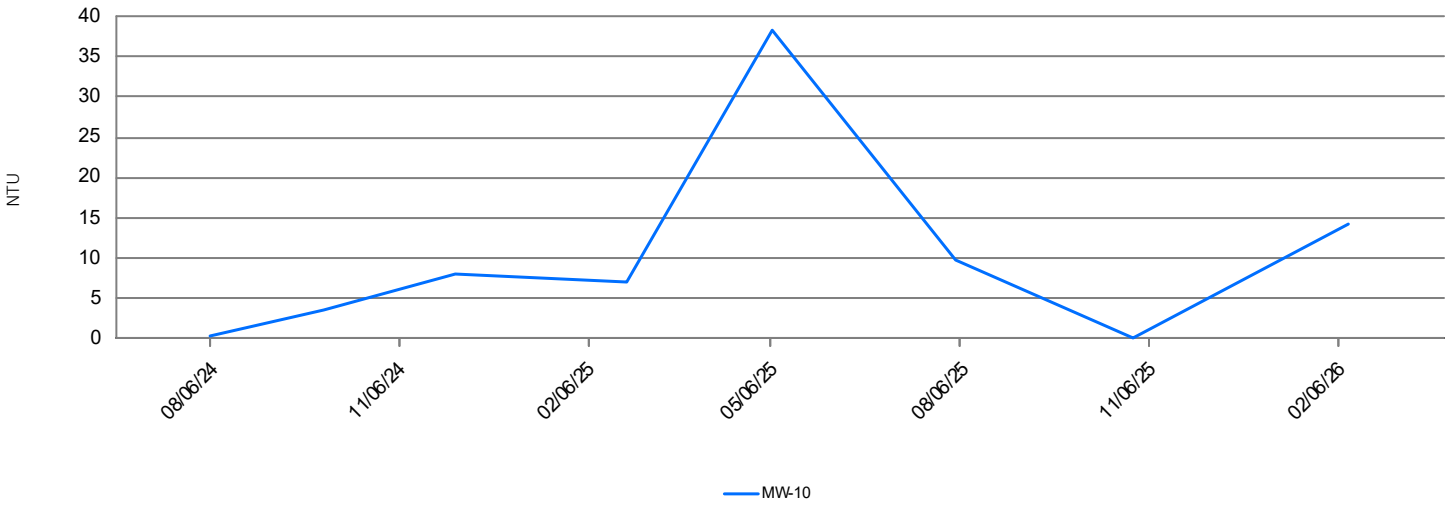
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

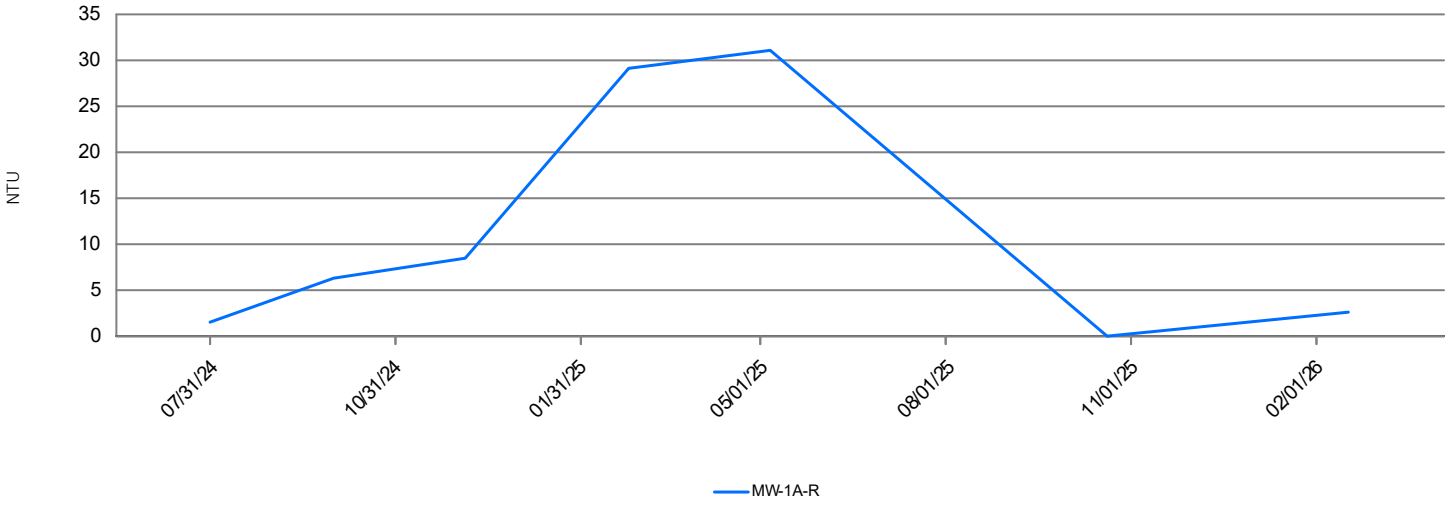
MonitorPro

No Group Selected, Turbidity (NTU)

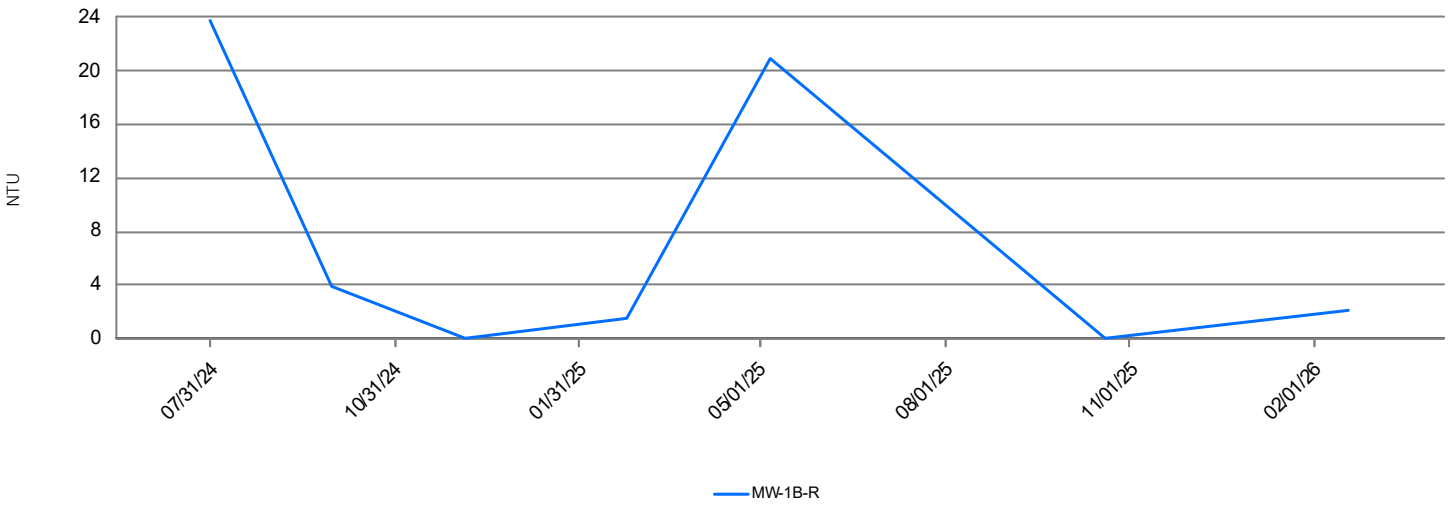
MW-10



MW-1A-R



MW-1B-R



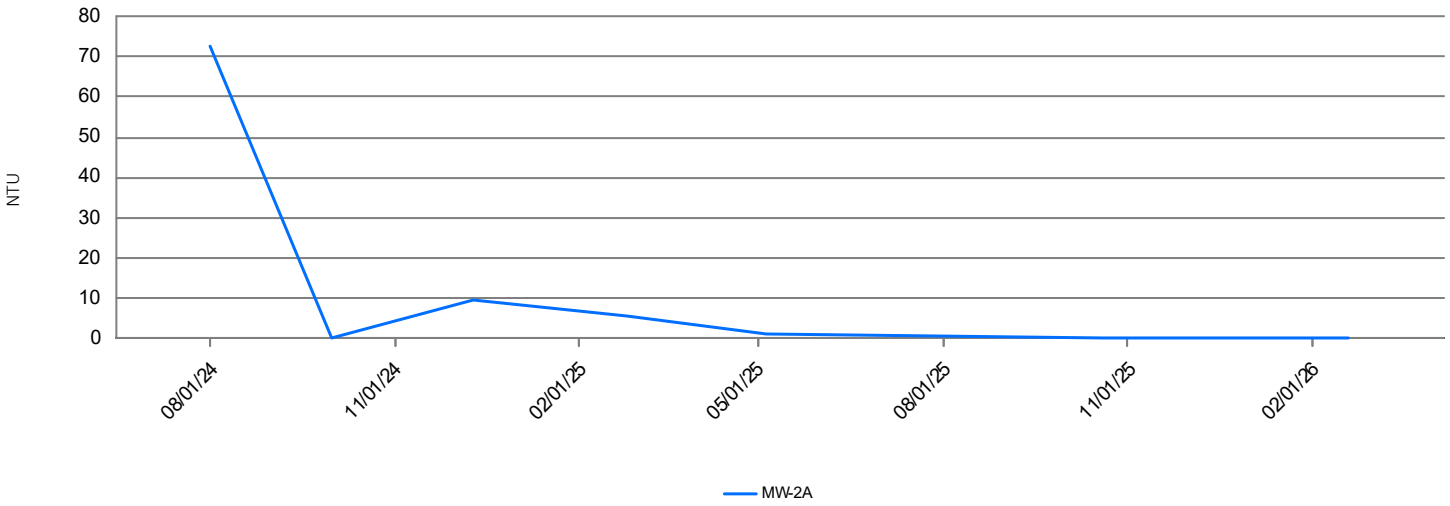
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

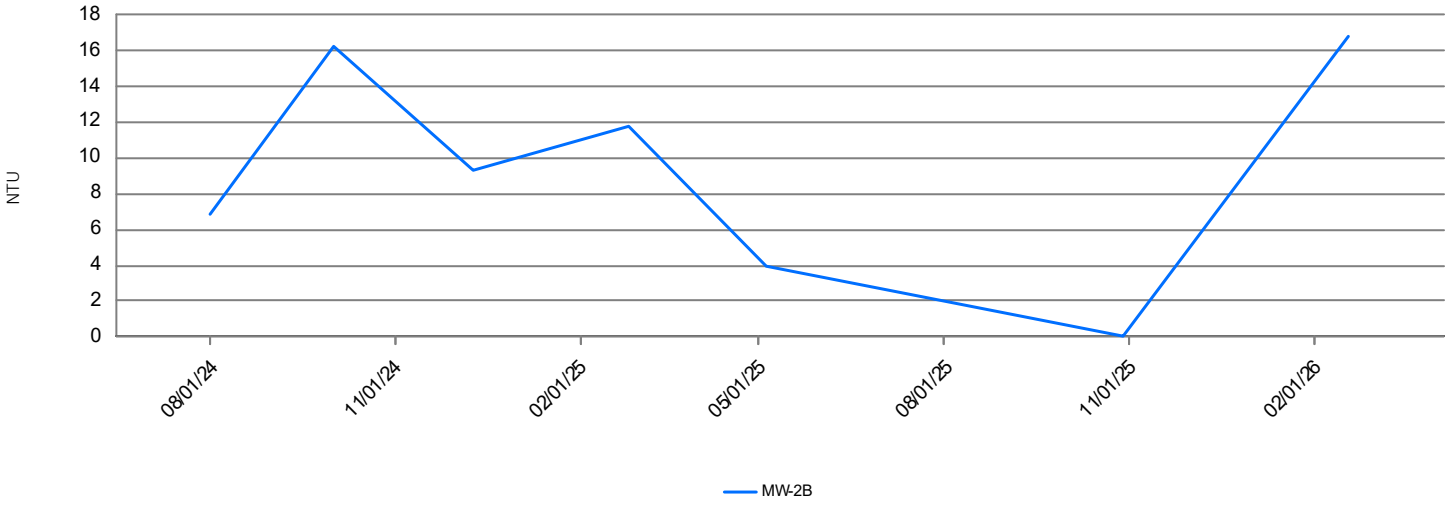
MonitorPro

No Group Selected, Turbidity (NTU)

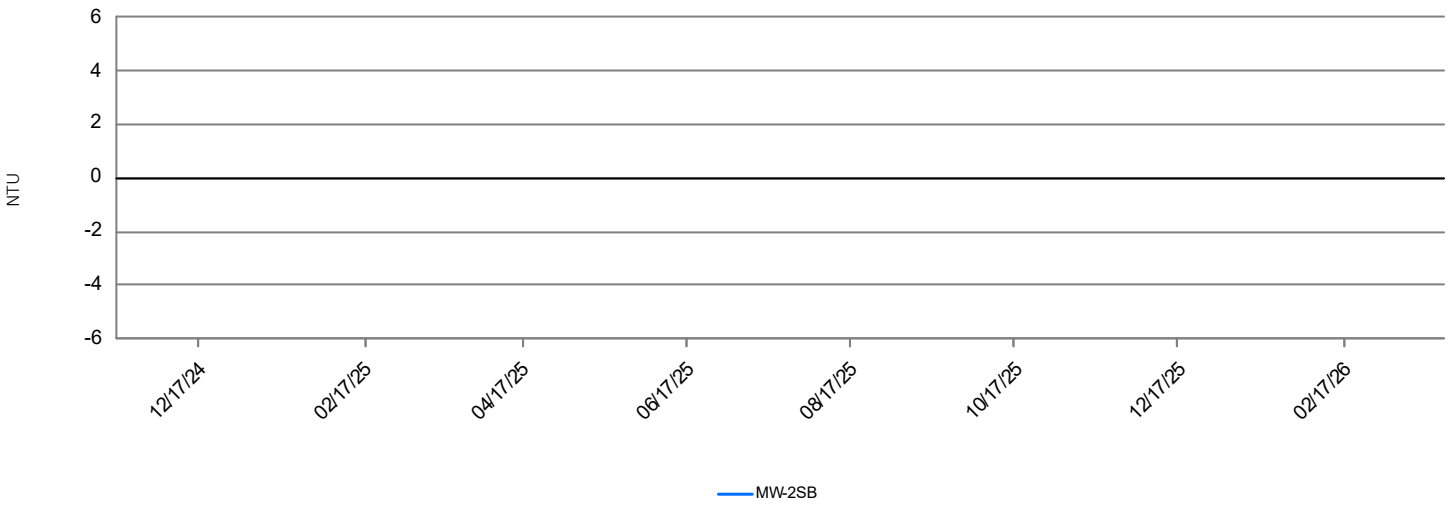
MW-2A



MW-2B



MW-2SB

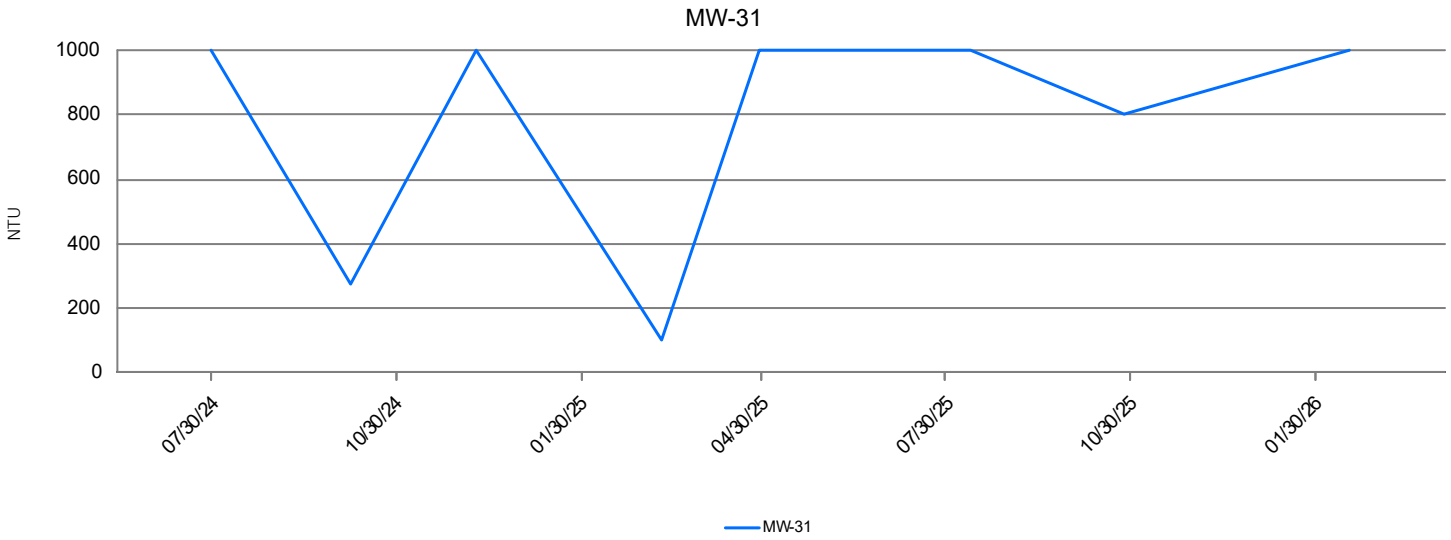


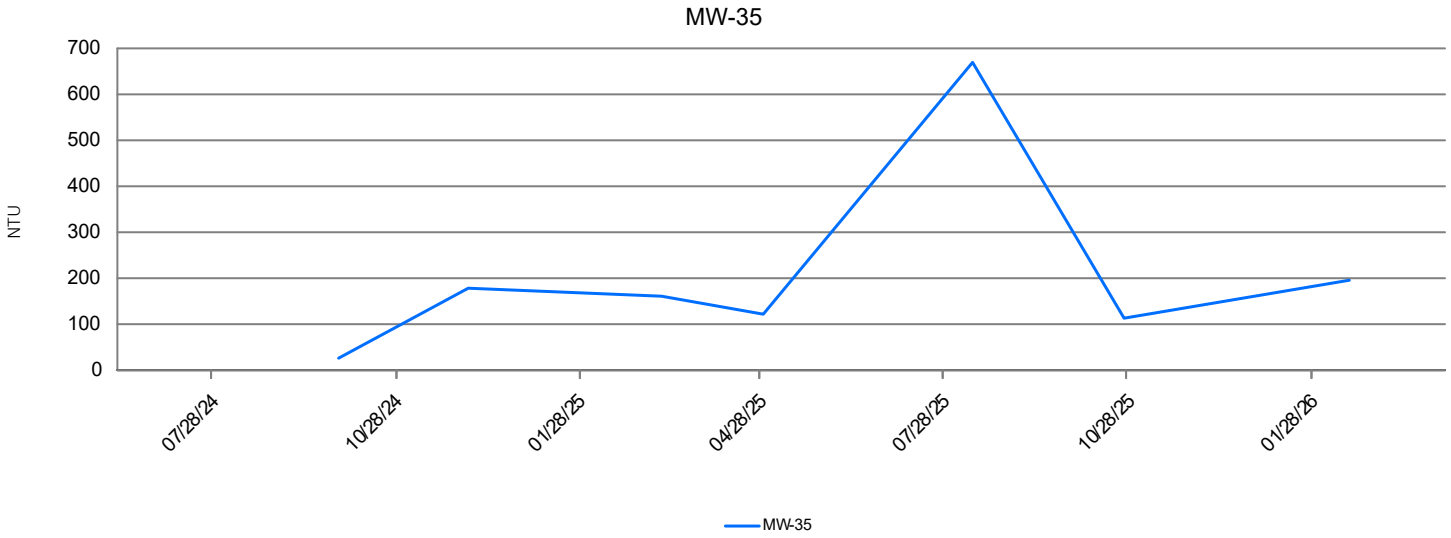
Variable Graphical Report

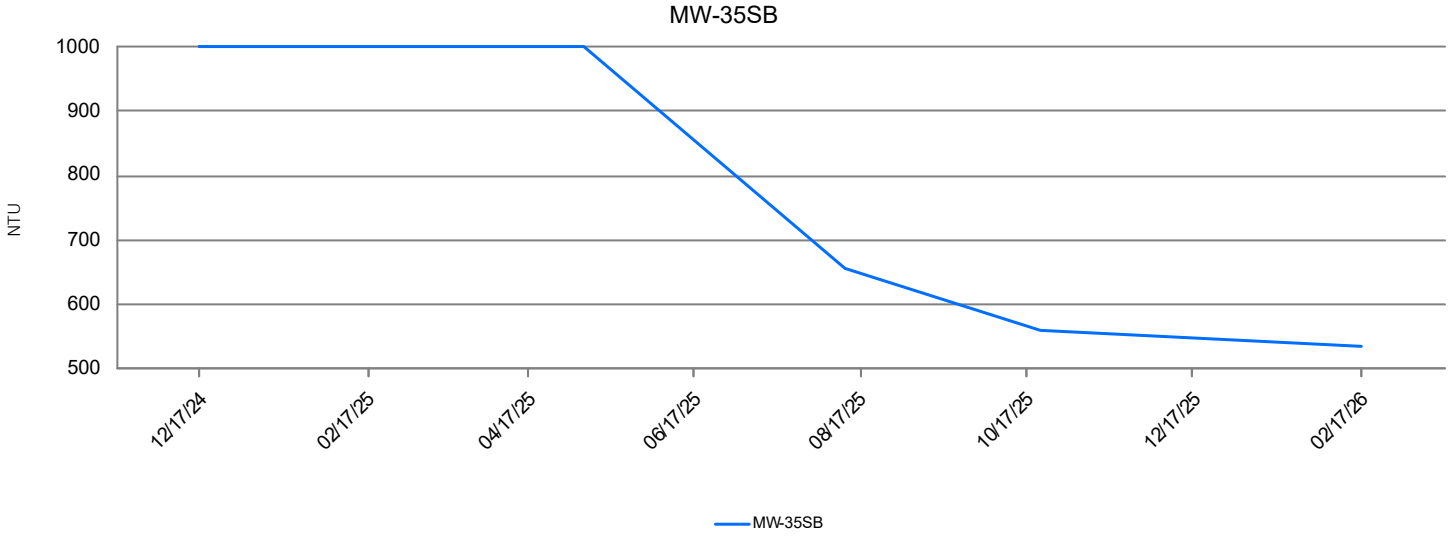
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Turbidity (NTU)





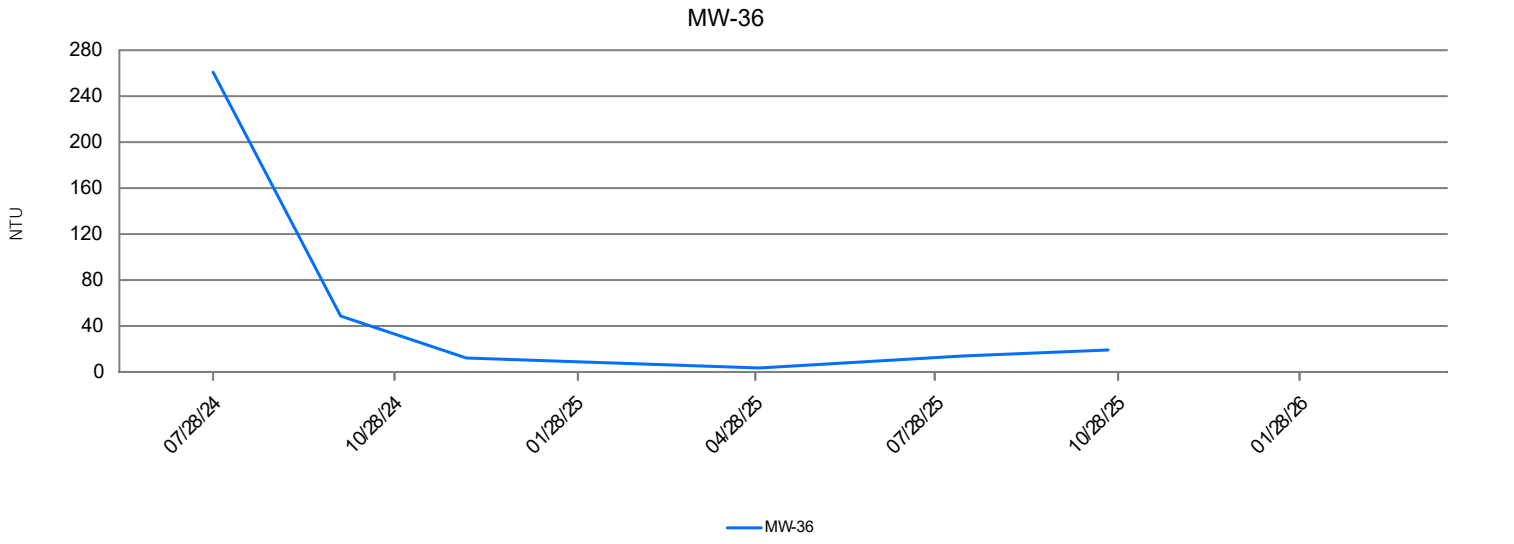


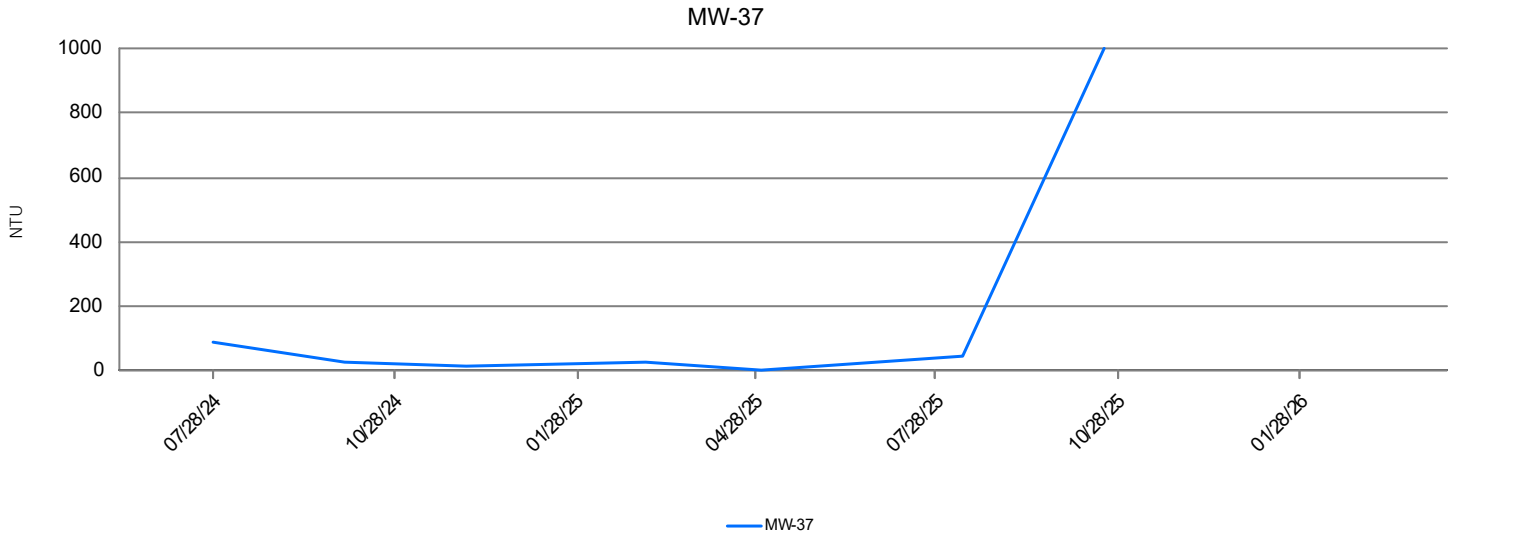
Variable Graphical Report

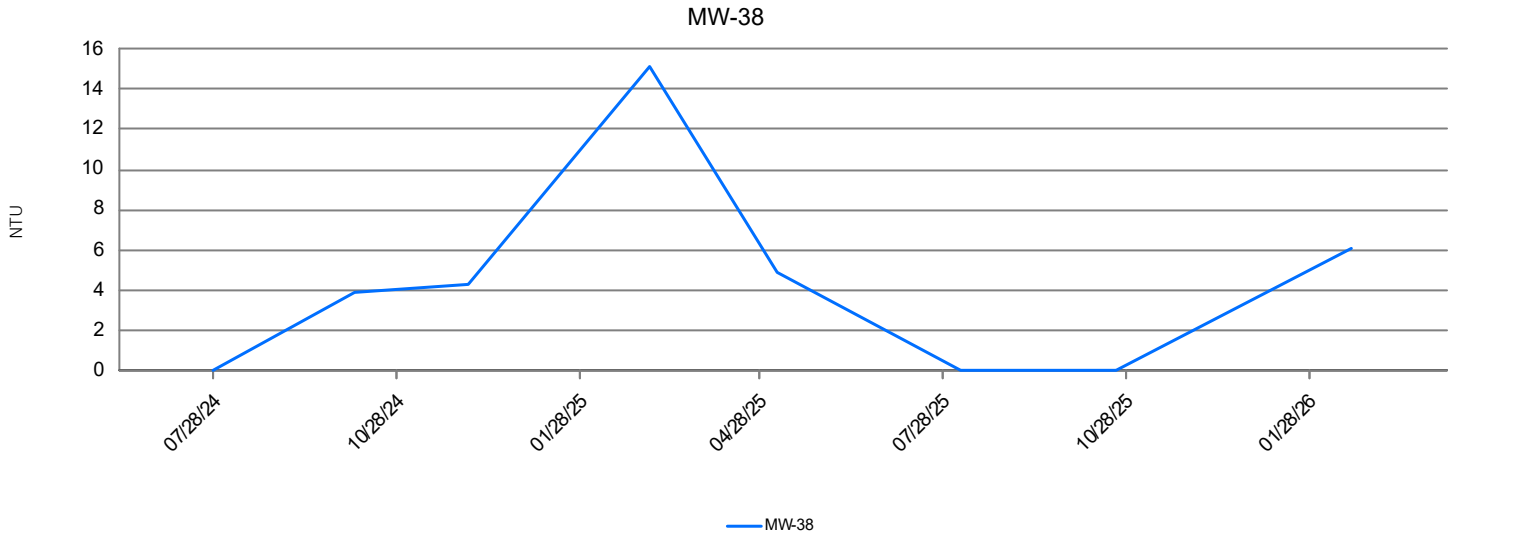
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Turbidity (NTU)







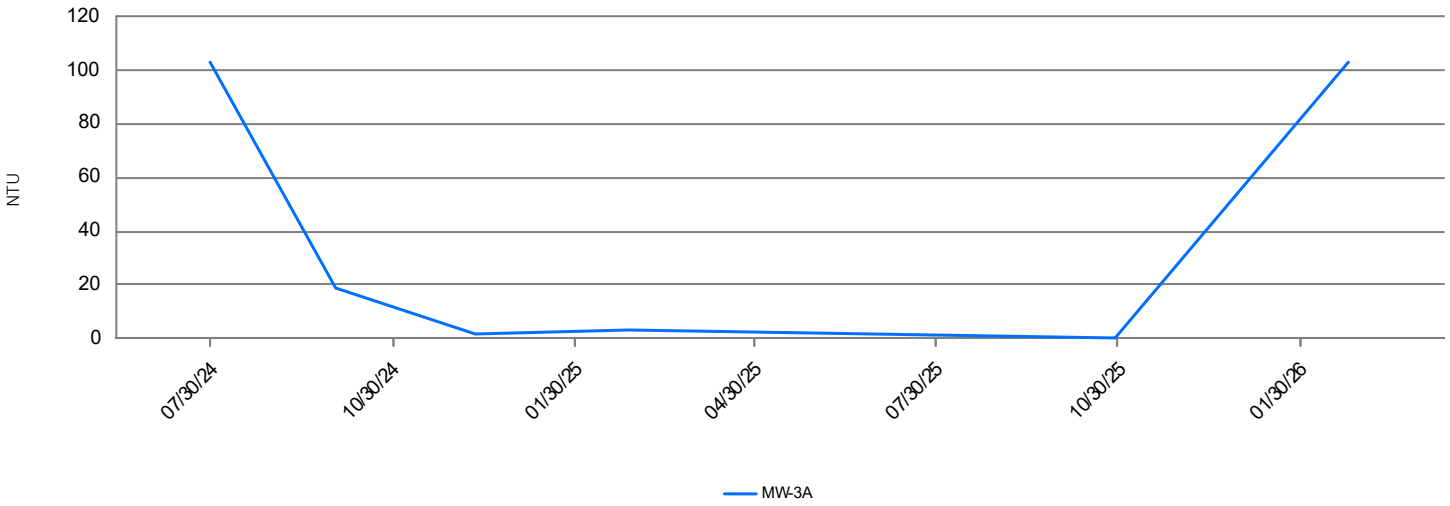
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

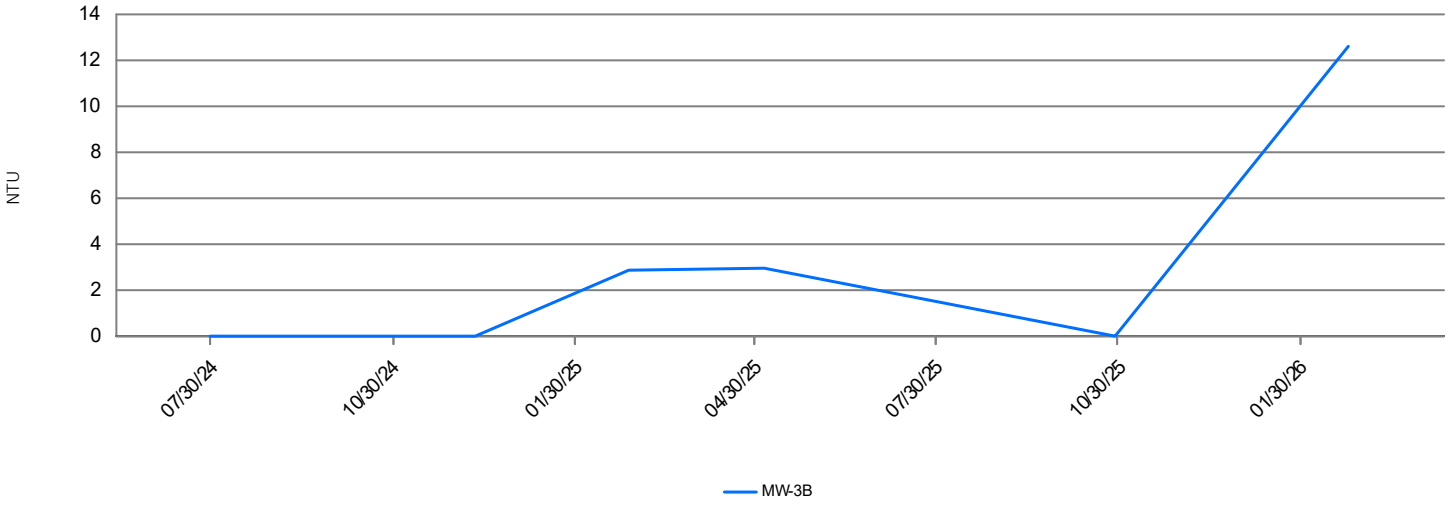
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No Group Selected, Turbidity (NTU)

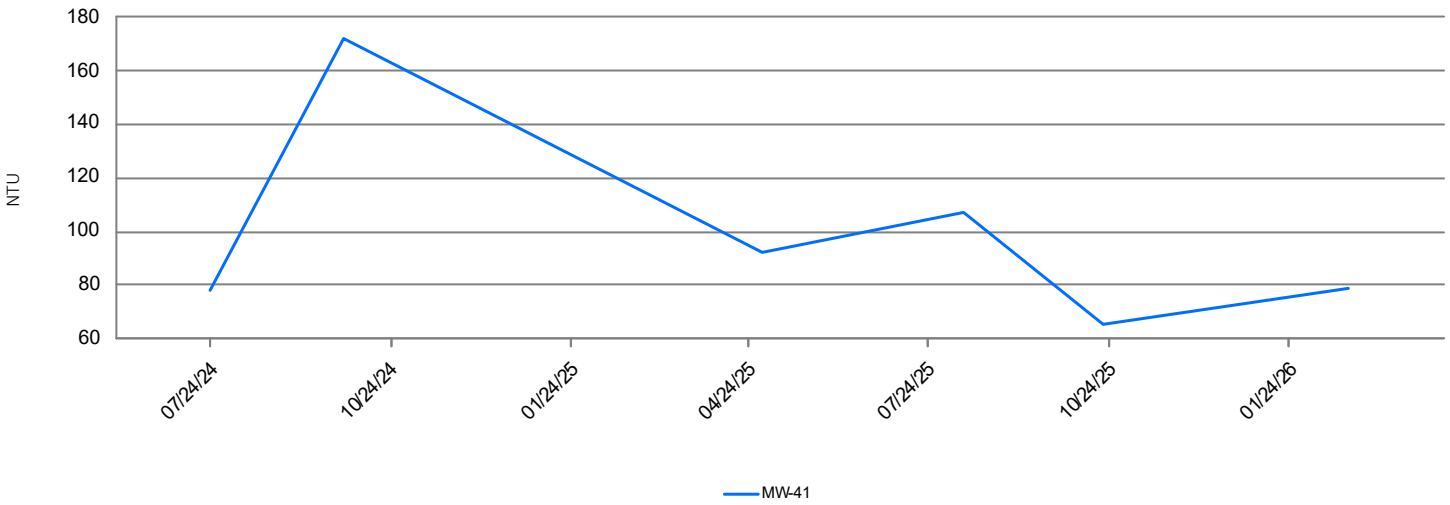
MW-3A



MW-3B



MW-41

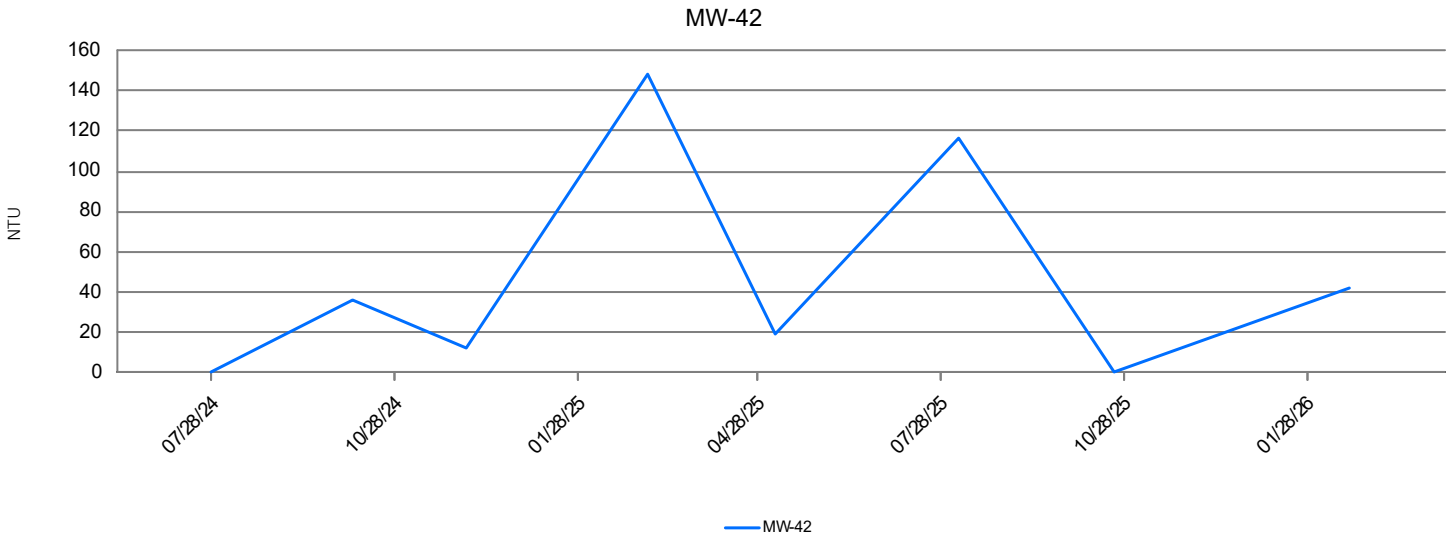


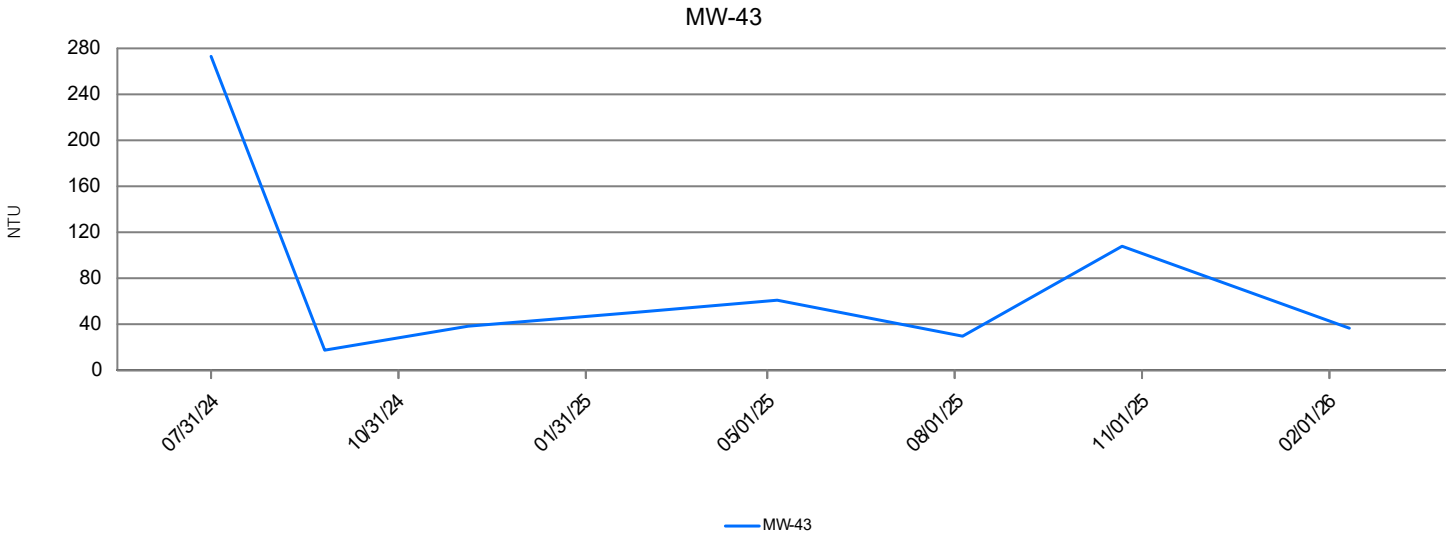
Variable Graphical Report

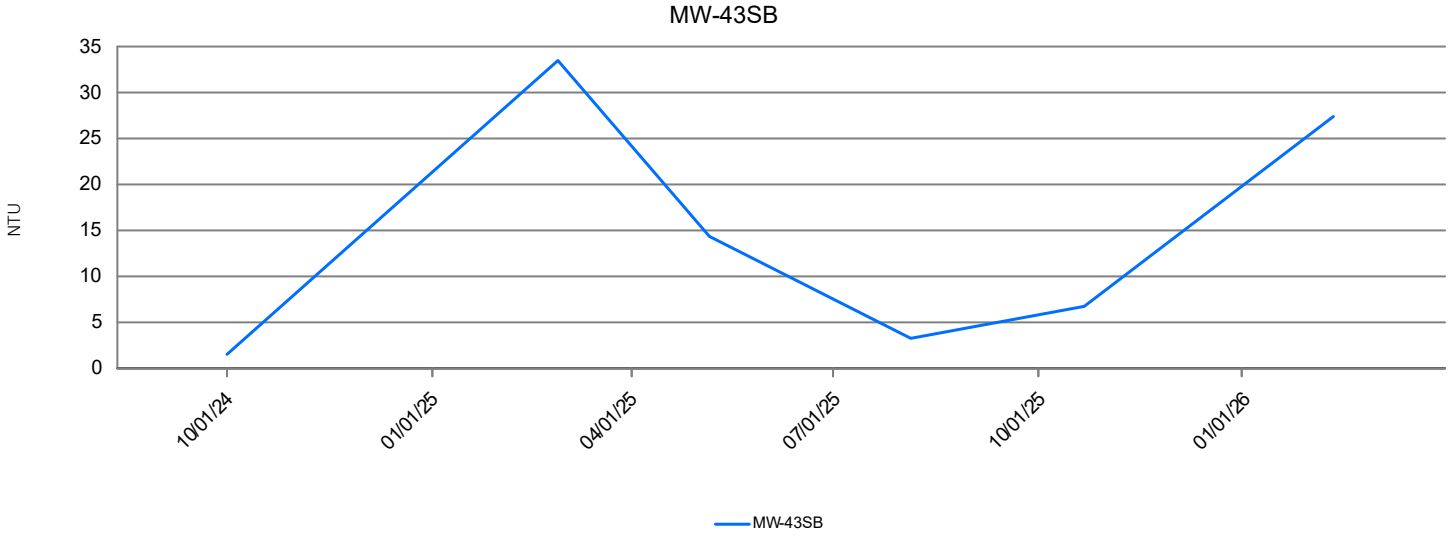
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Turbidity (NTU)





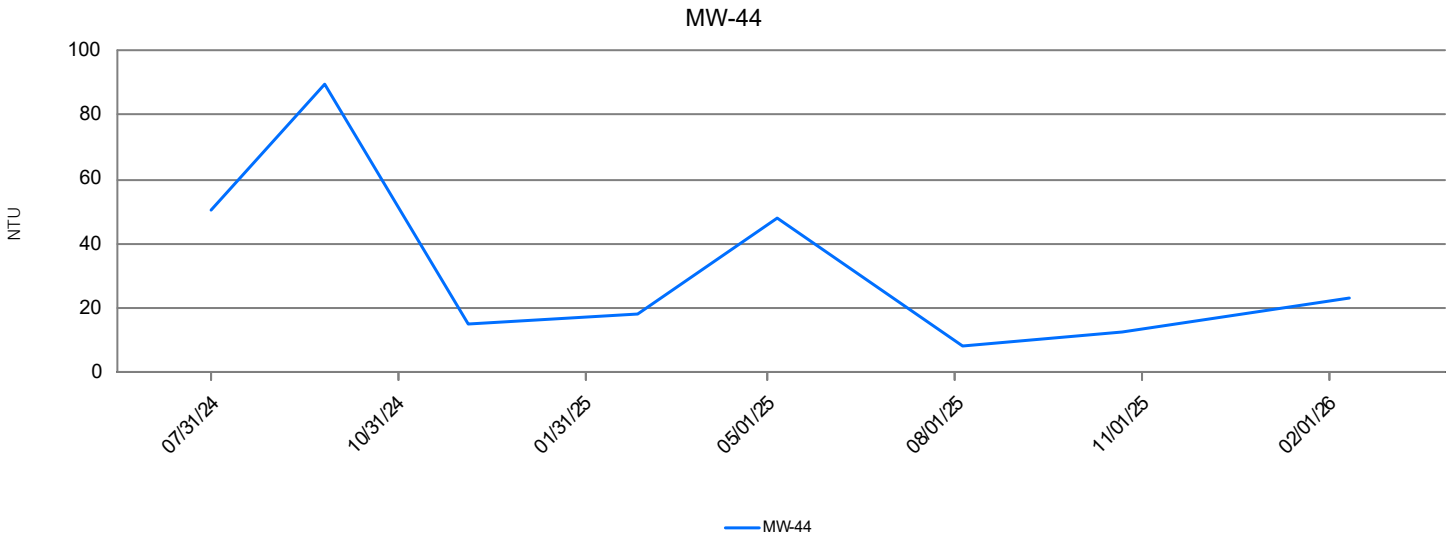


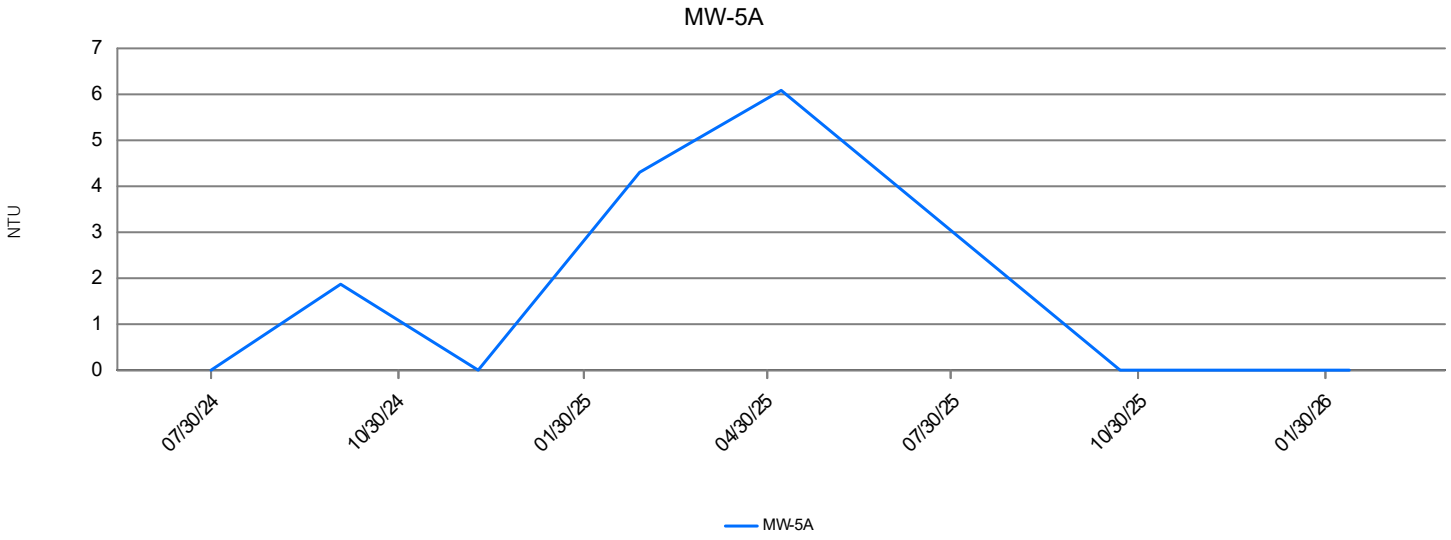
Variable Graphical Report

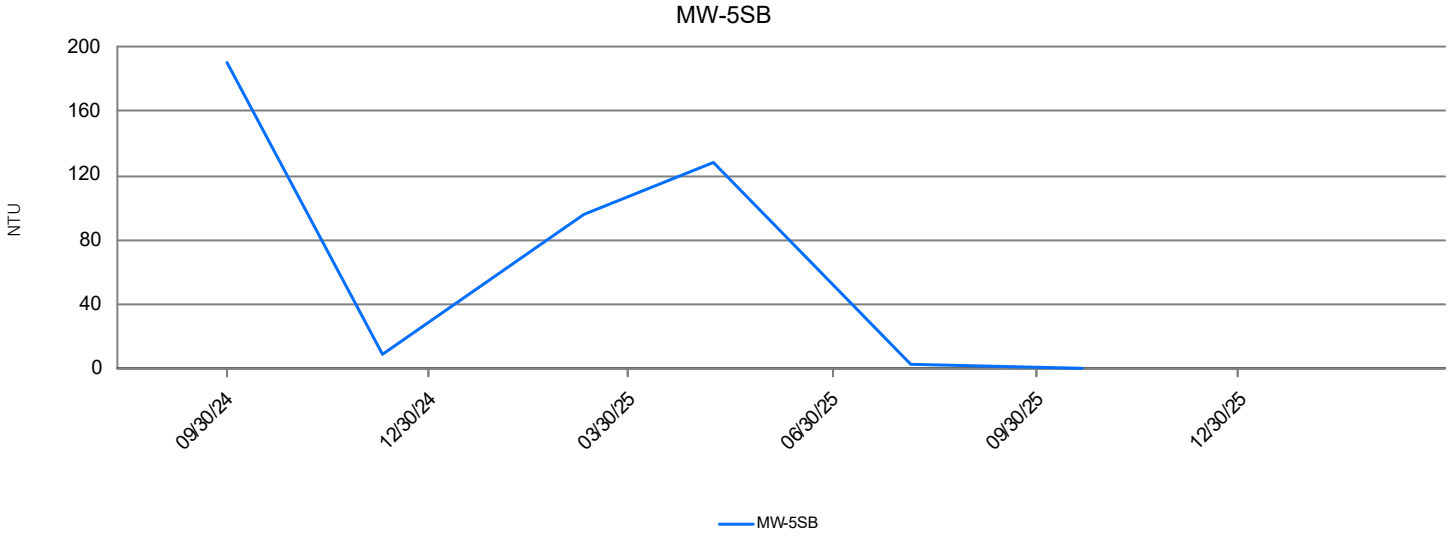
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Turbidity (NTU)







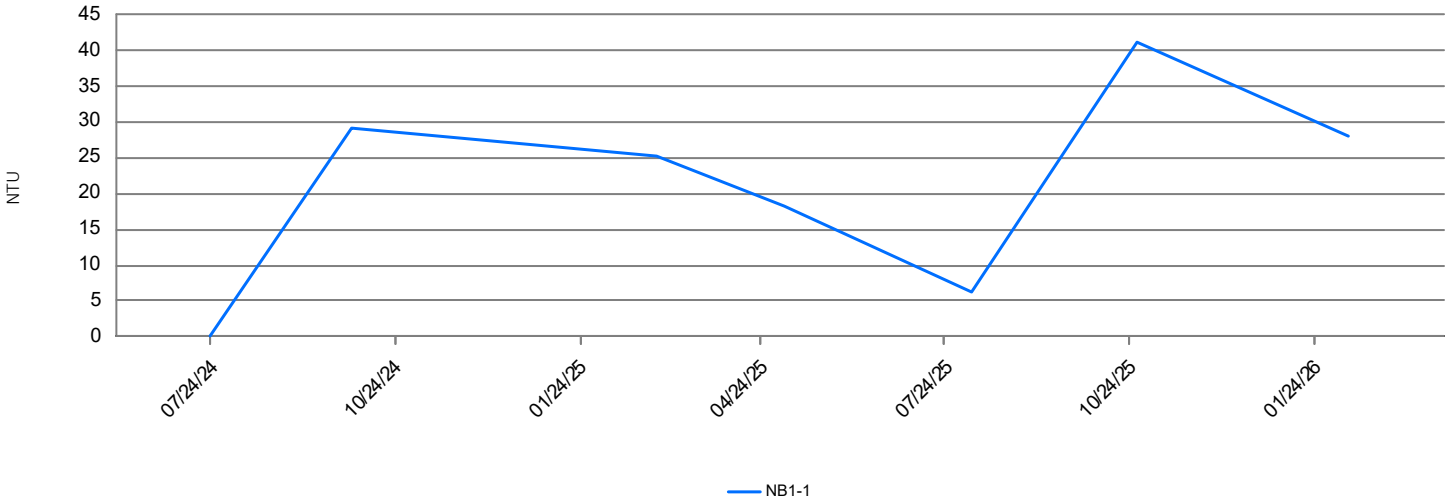
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

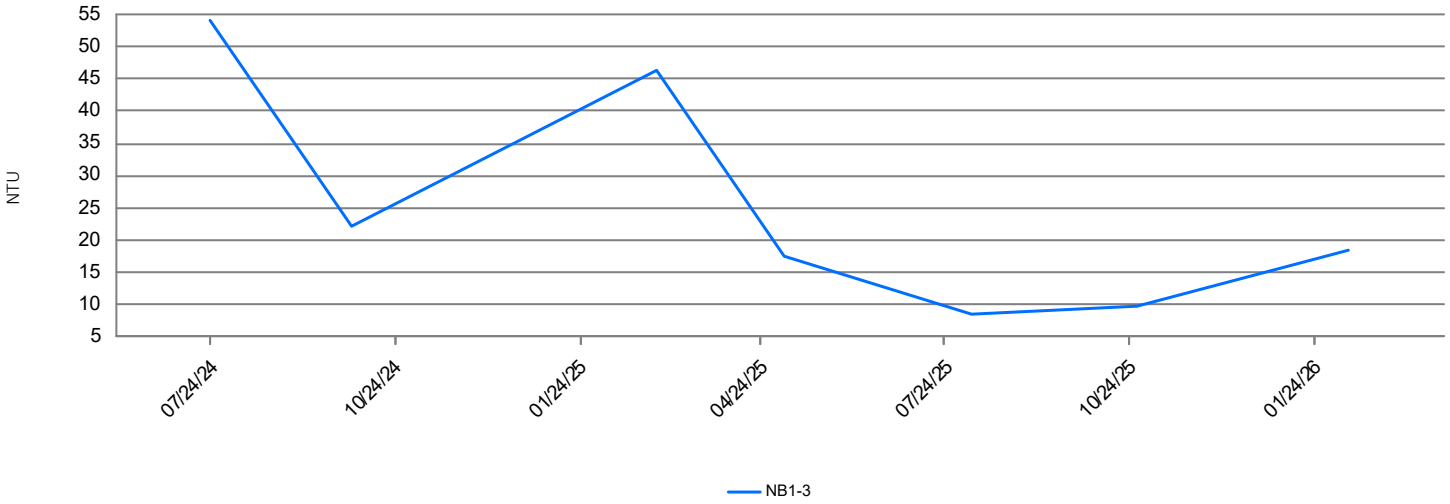
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No Group Selected, Turbidity (NTU)

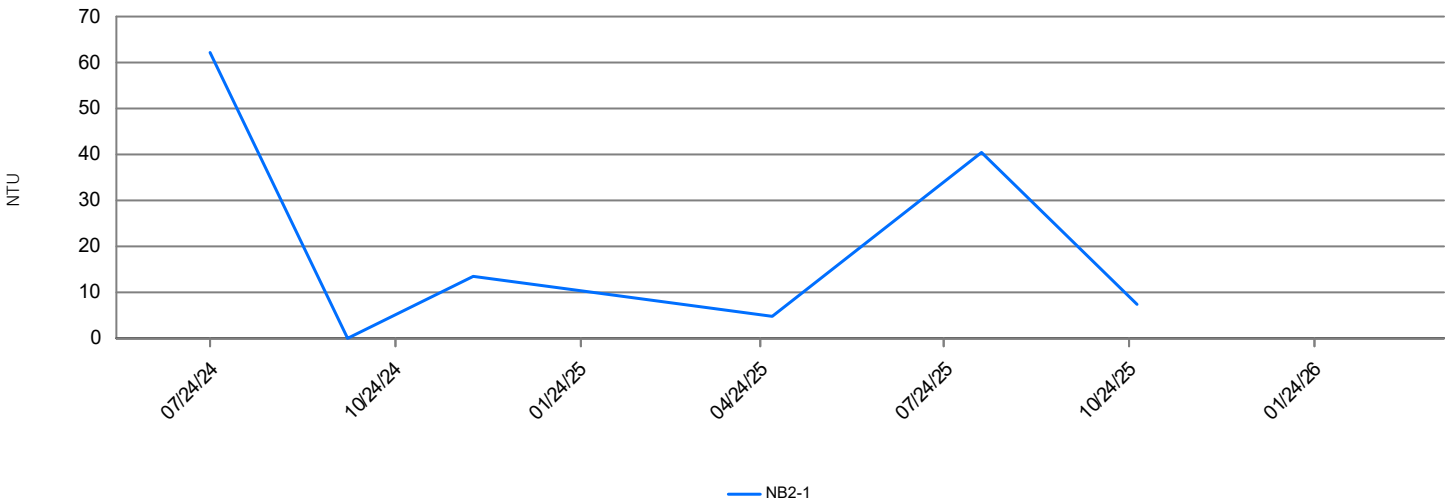
NB1-1



NB1-3



NB2-1



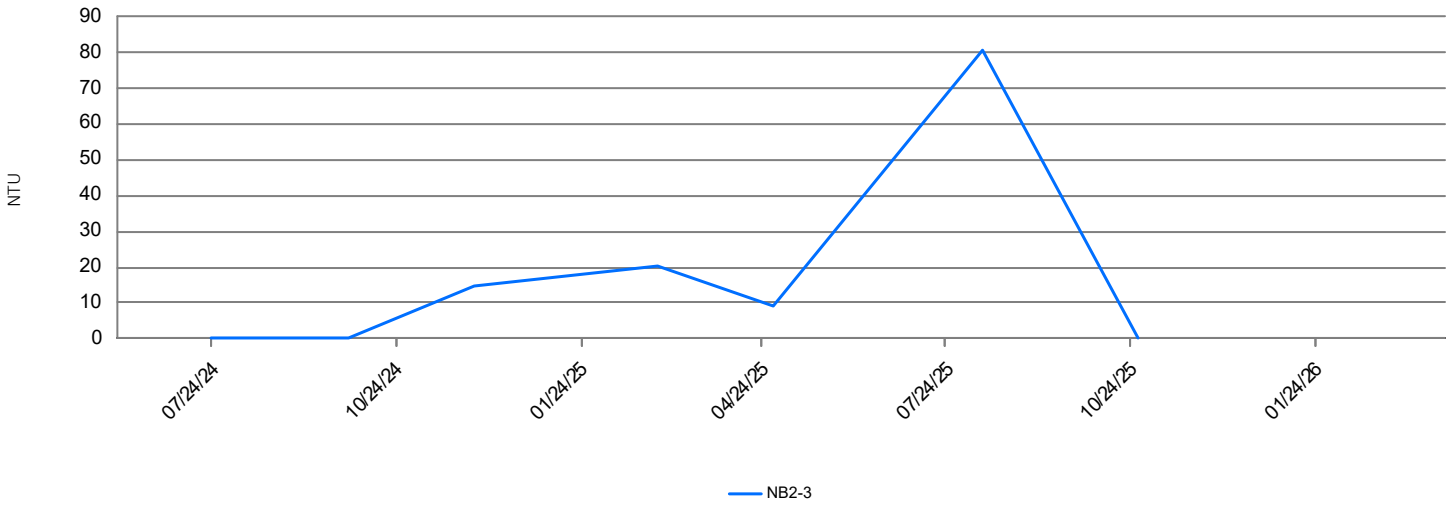
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

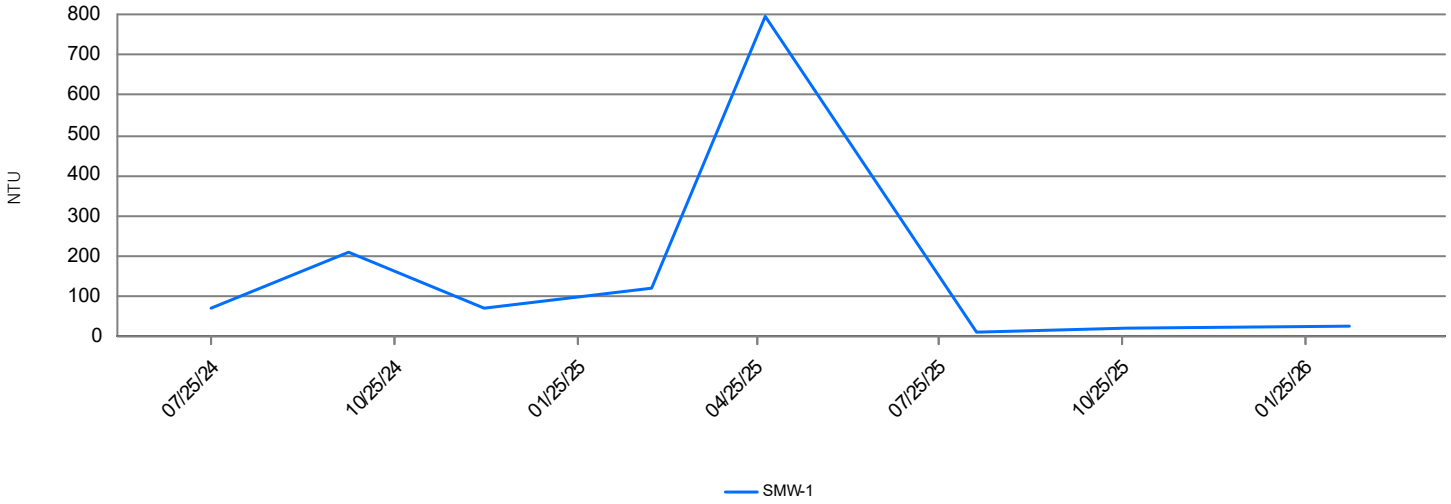
MonitorPro

No Group Selected, Turbidity (NTU)

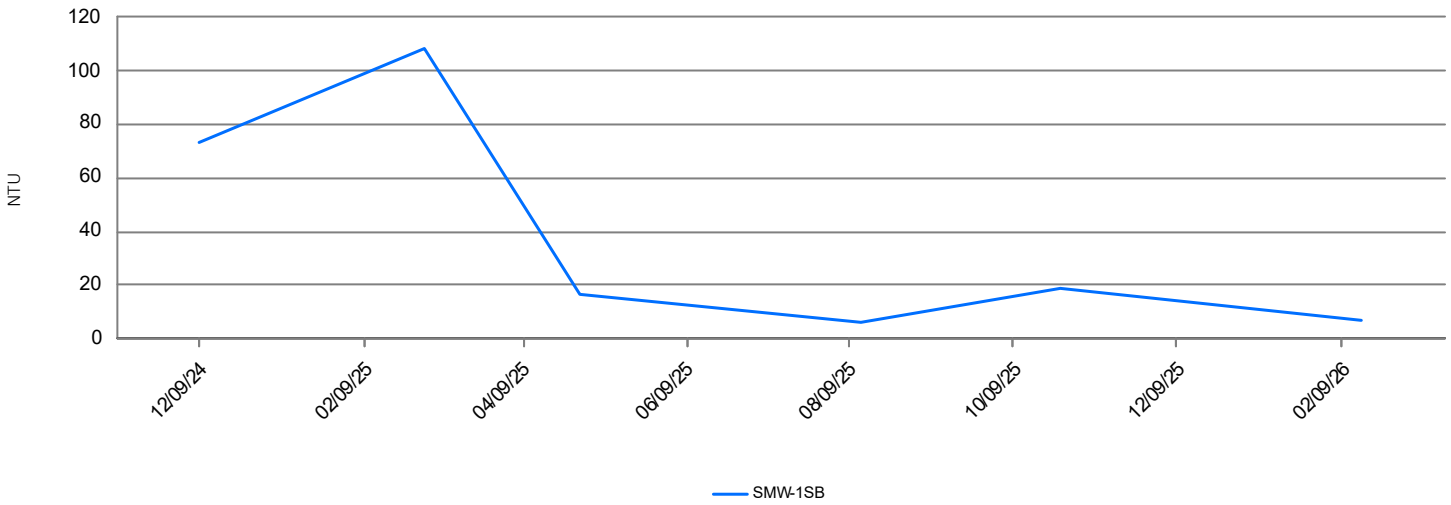
NB2-3



SMW-1



SMW-1SB



Printed Date: 05/21/2026

EHS DATA

MCERTS Cert. no. Sira MC090140/02

MCERTS

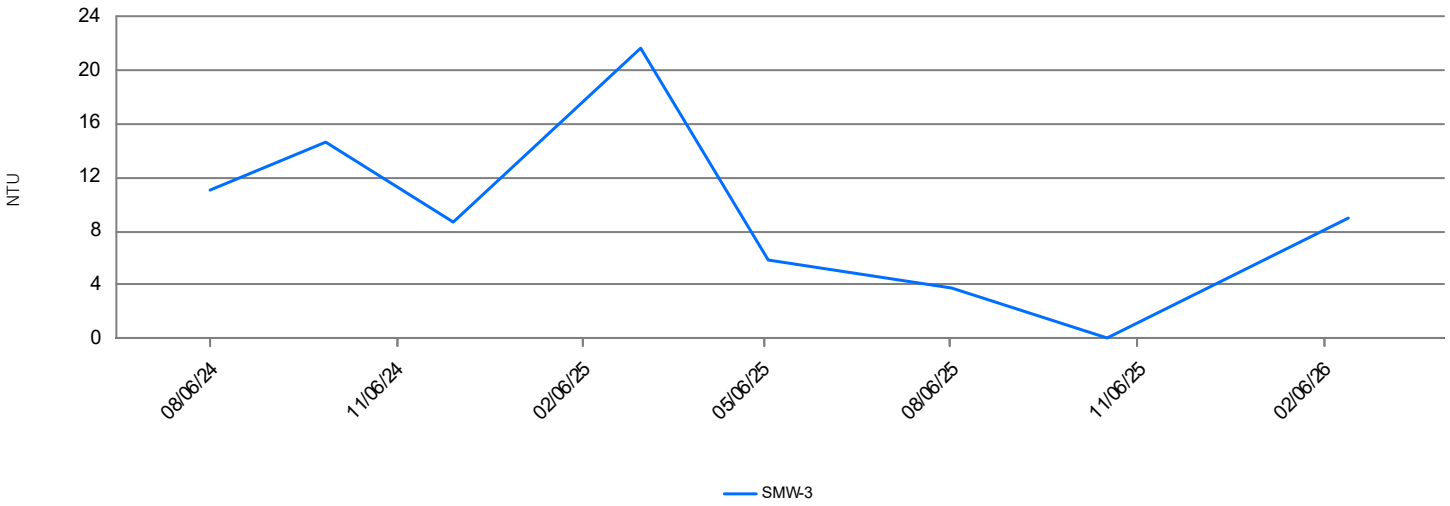
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

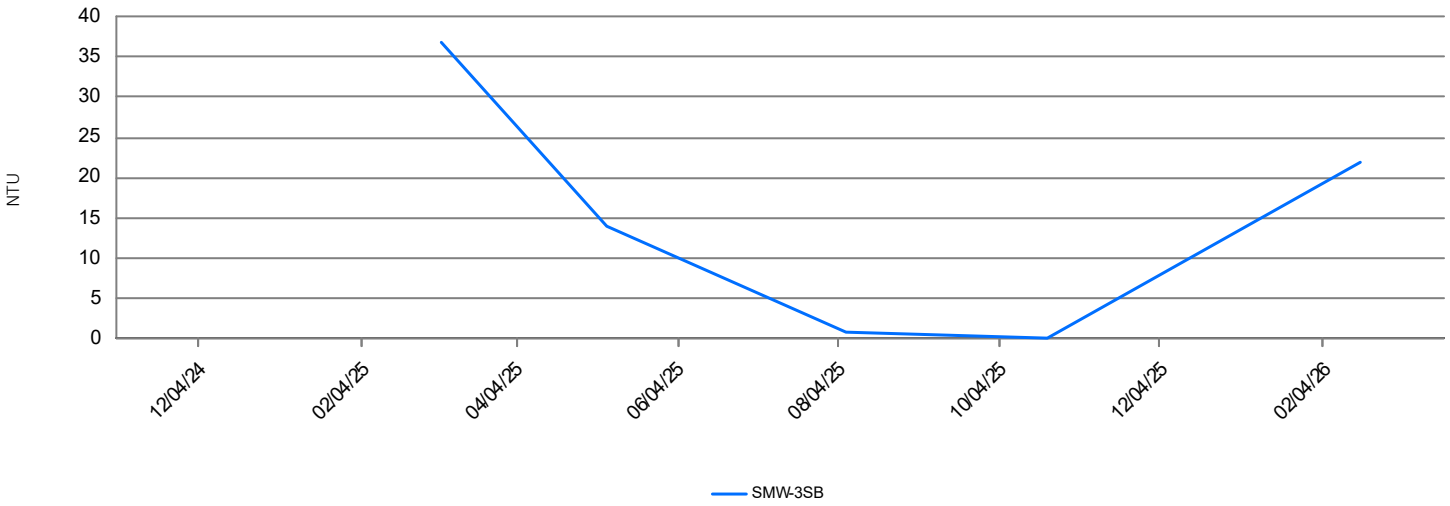
MonitorPro

No Group Selected, Turbidity (NTU)

SMW-3



SMW-3SB

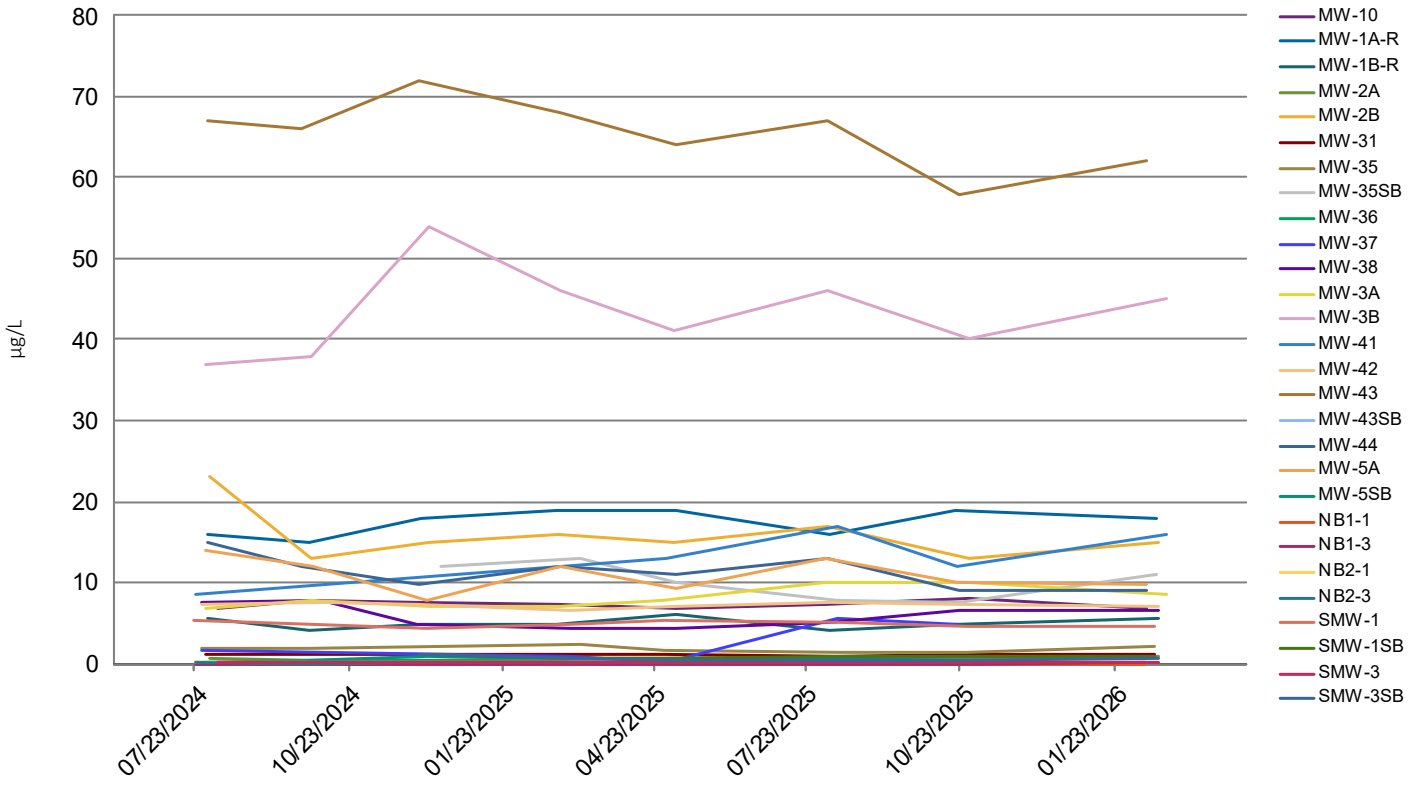


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Uranium, Dissolved (µg/L)

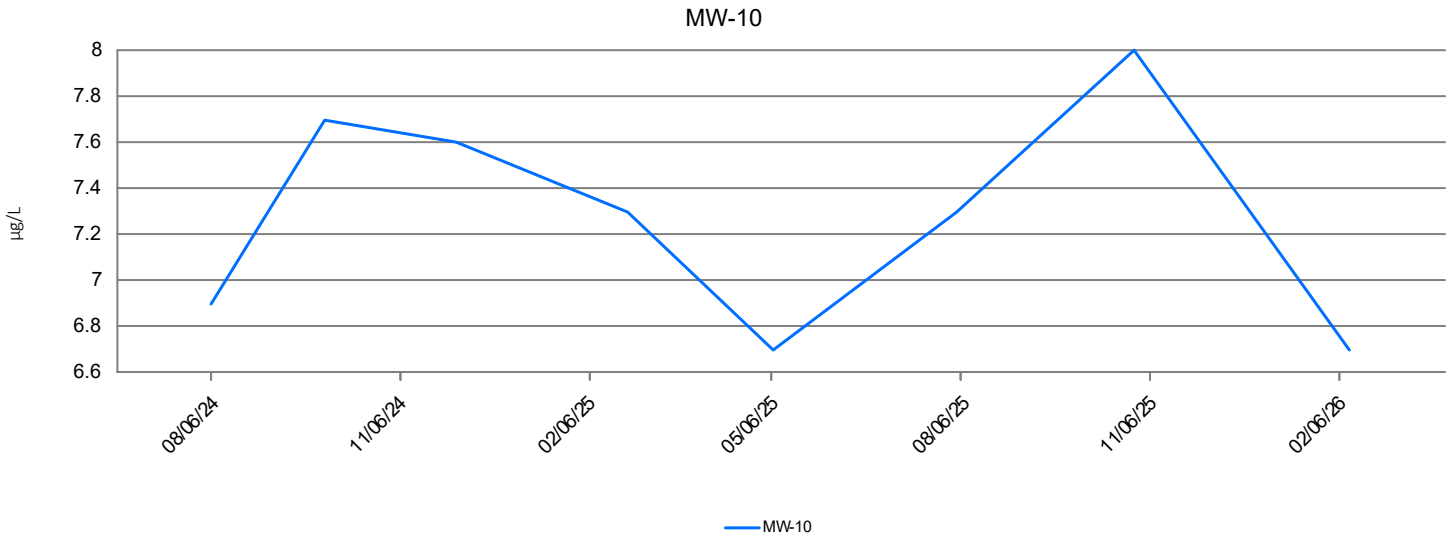


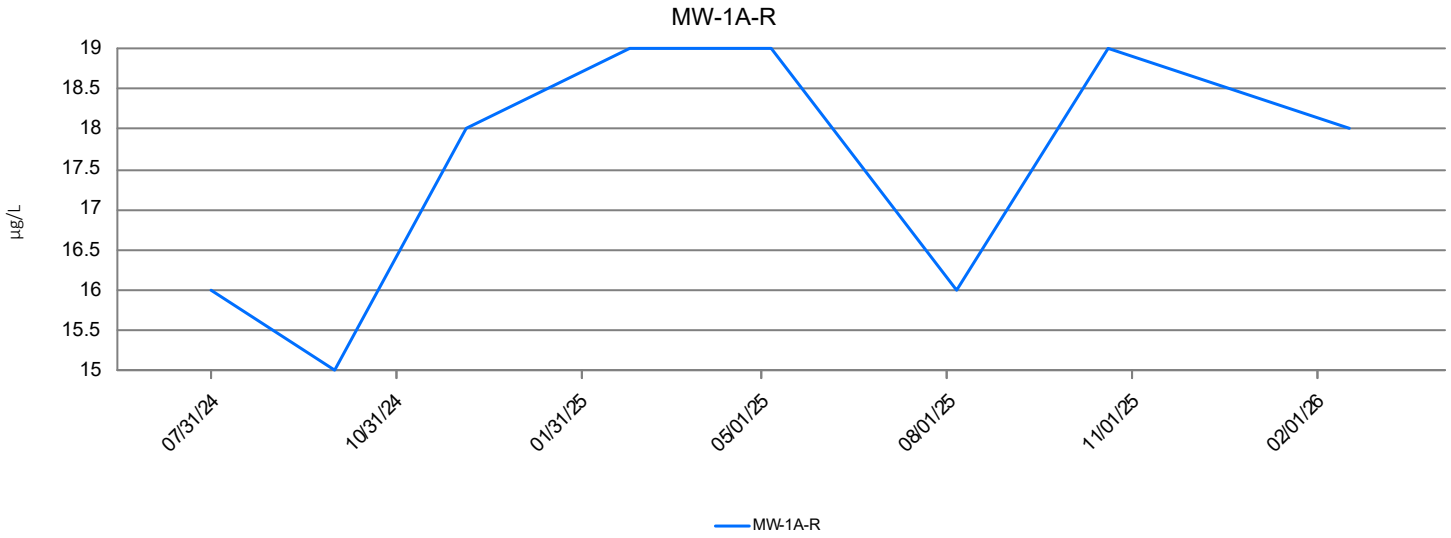
Variable Graphical Report

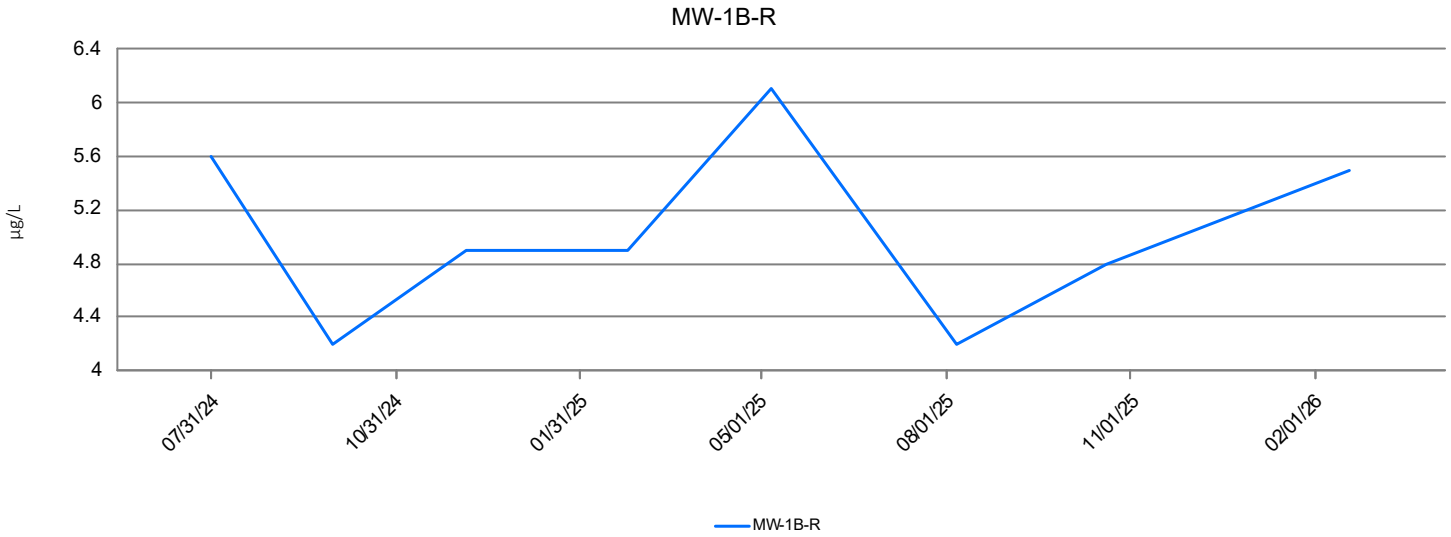
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Uranium, Dissolved (µg/L)







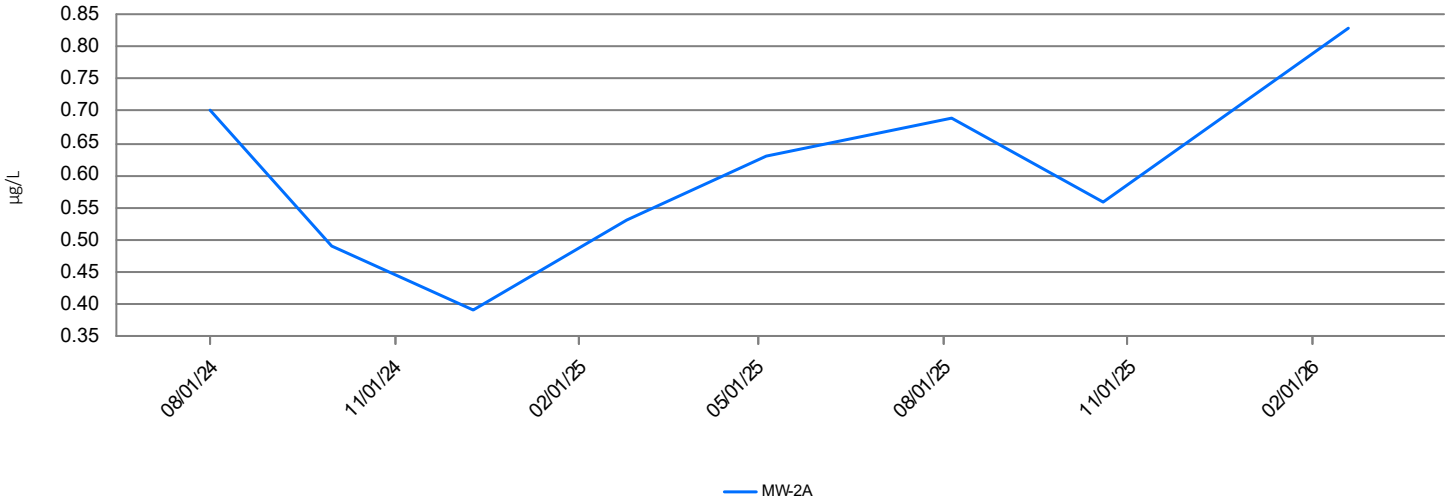
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

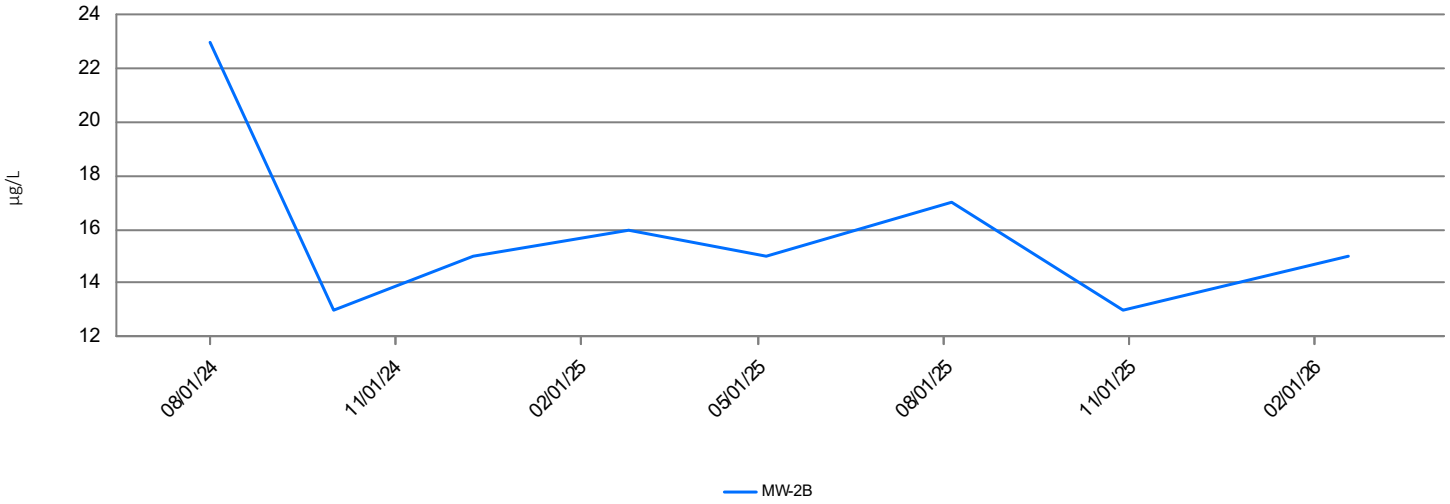
MonitorPro

No Group Selected, Uranium, Dissolved (µg/L)

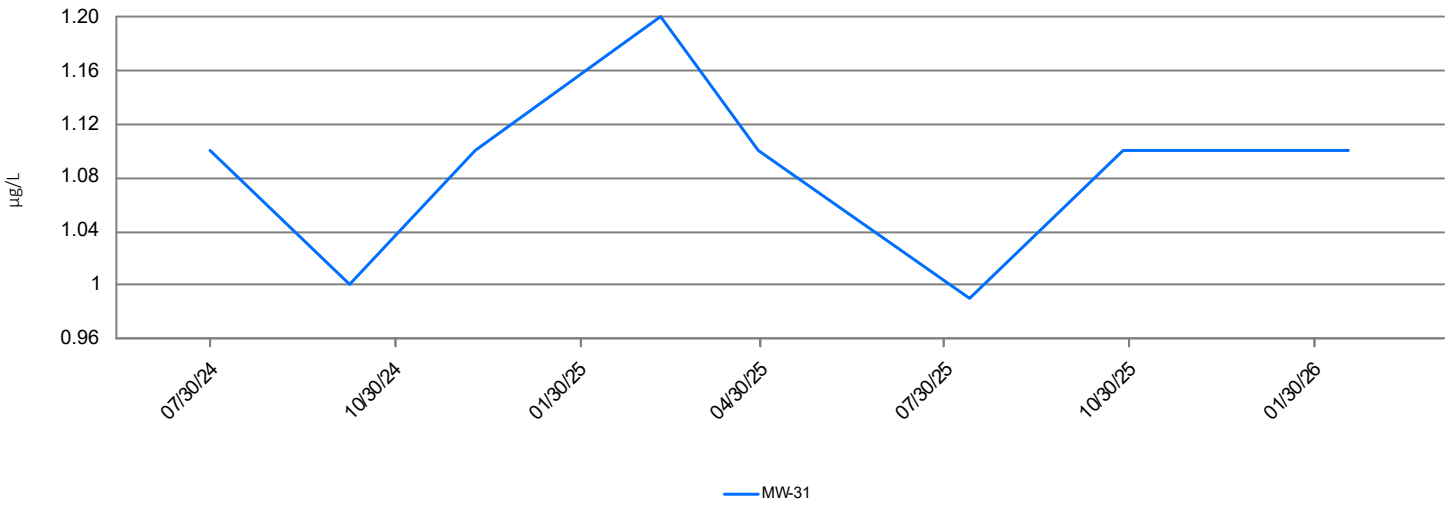
MW-2A



MW-2B



MW-31

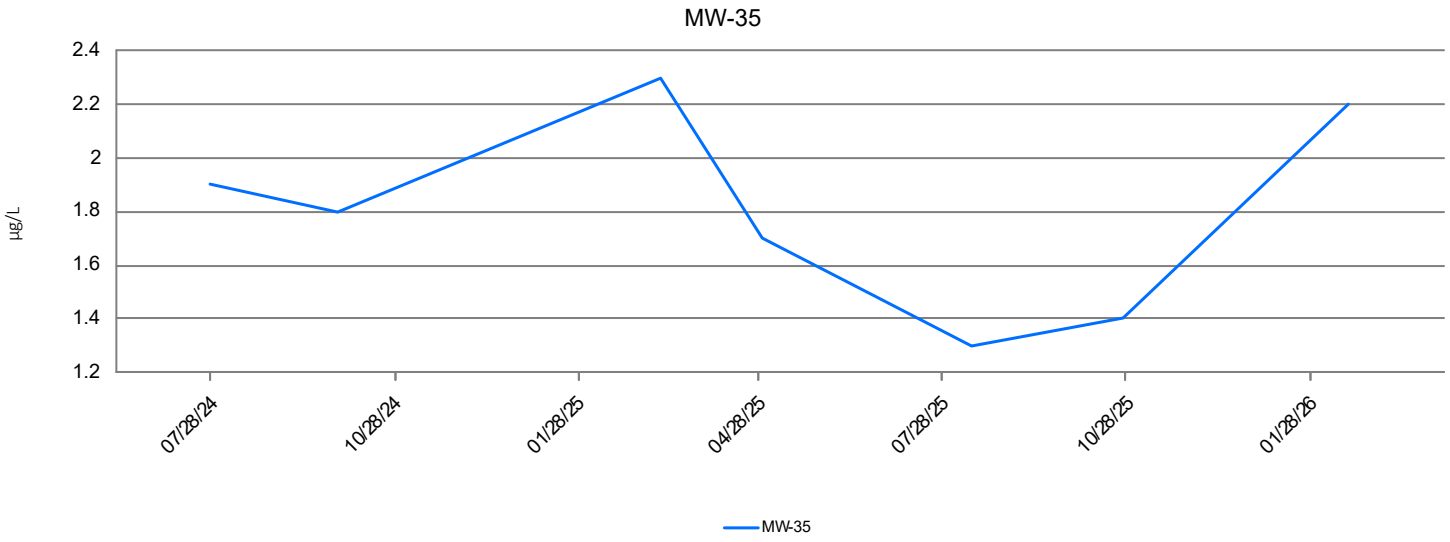


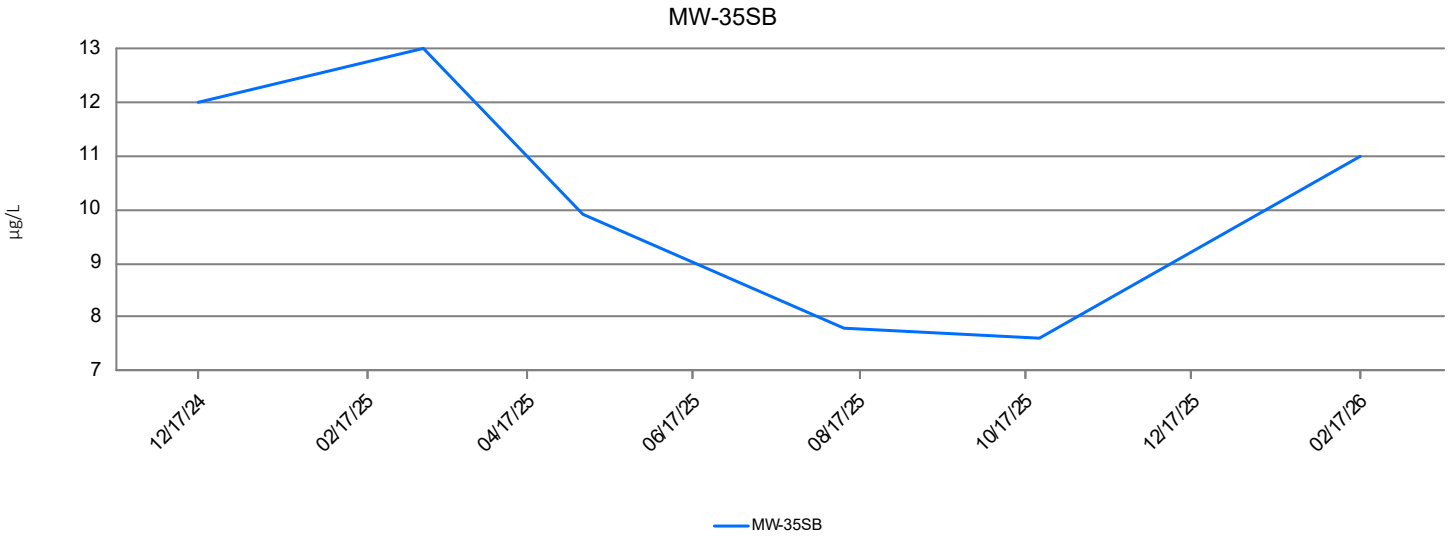
Variable Graphical Report

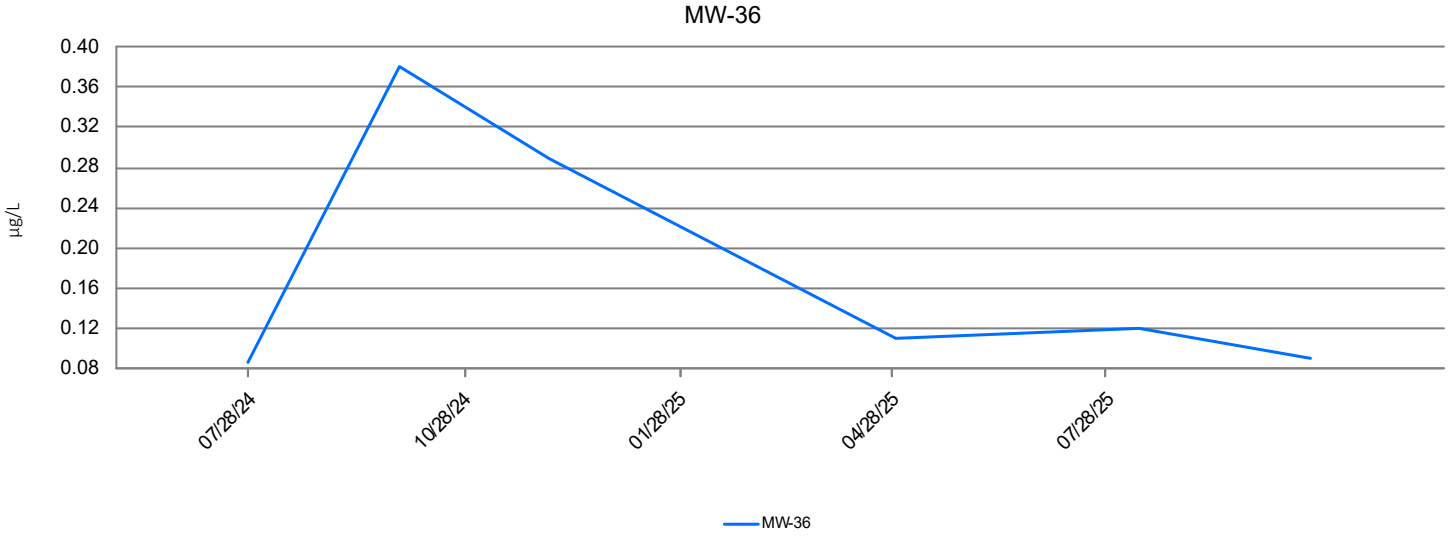
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Uranium, Dissolved (µg/L)





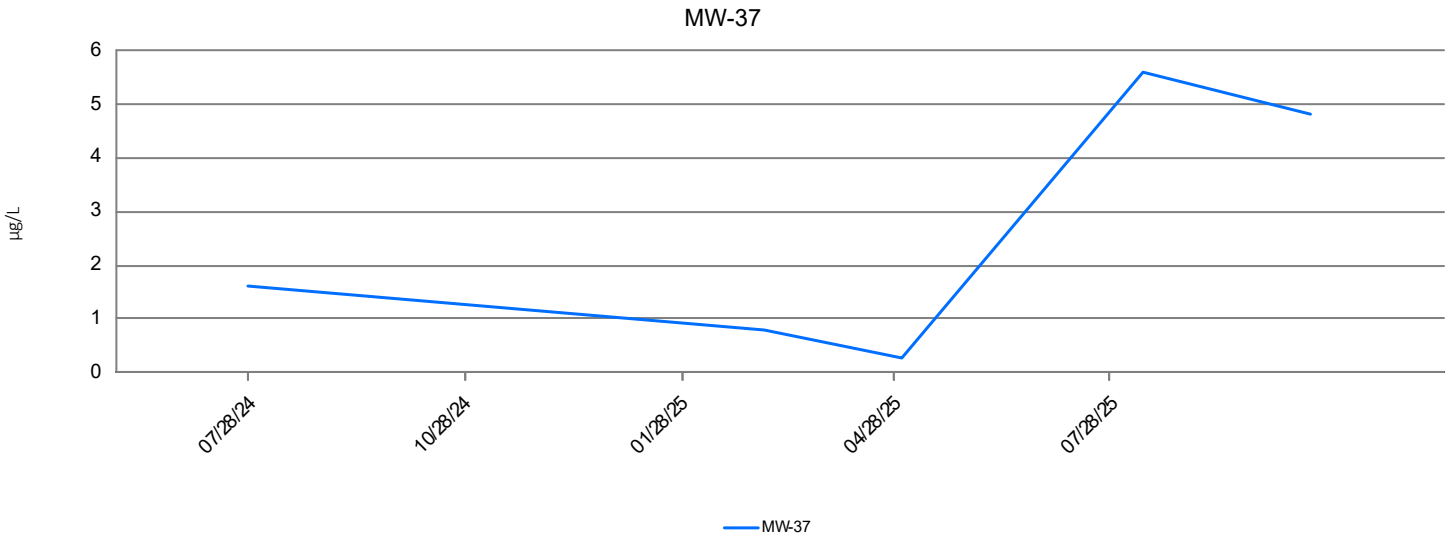


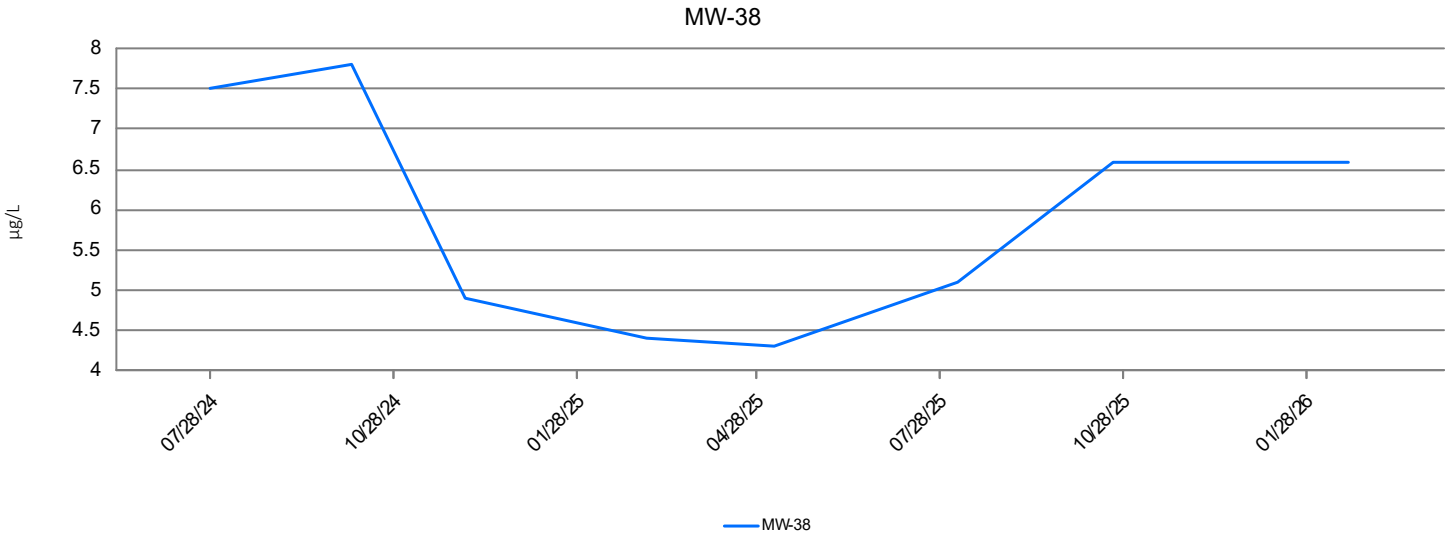
Variable Graphical Report

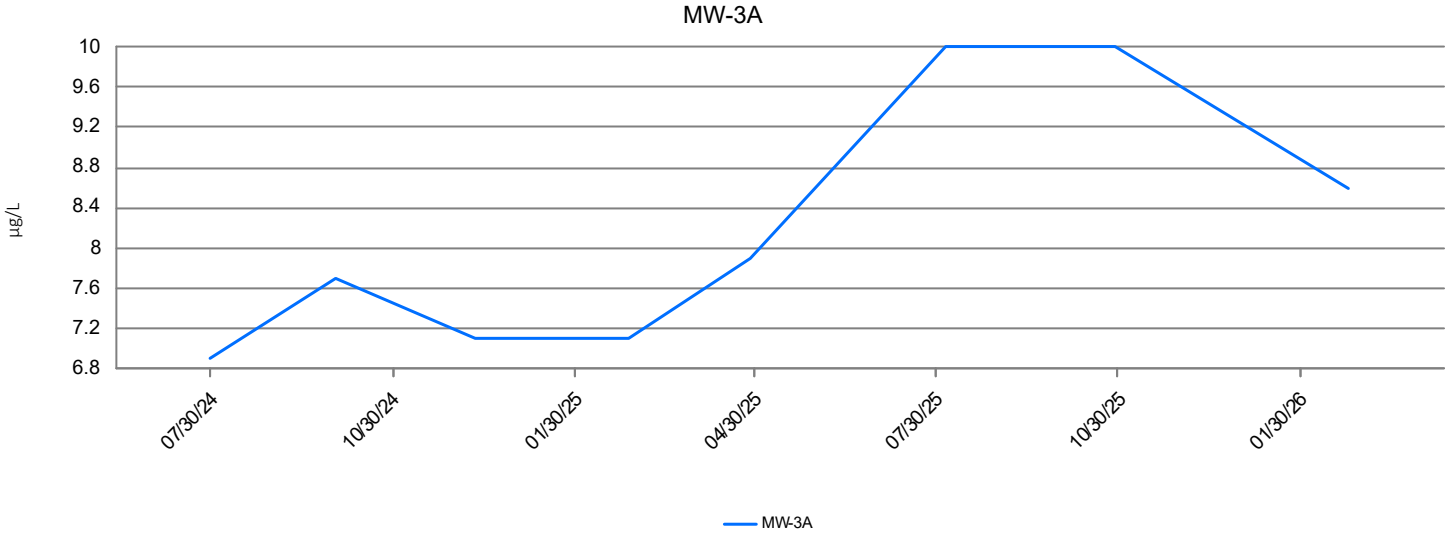
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Uranium, Dissolved (µg/L)







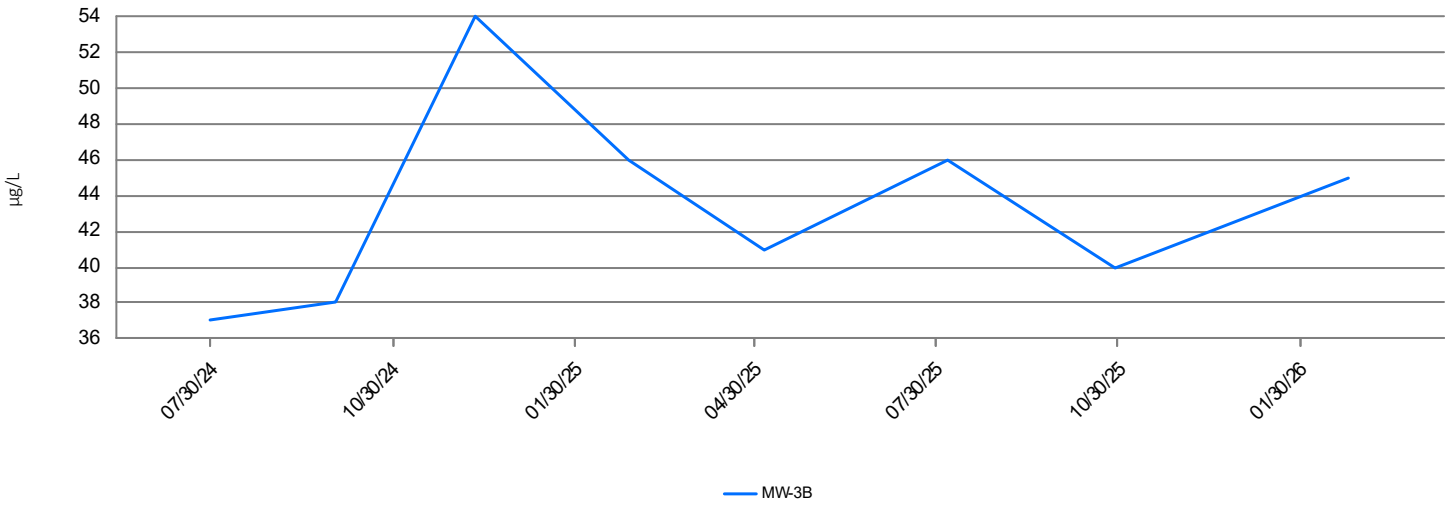
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

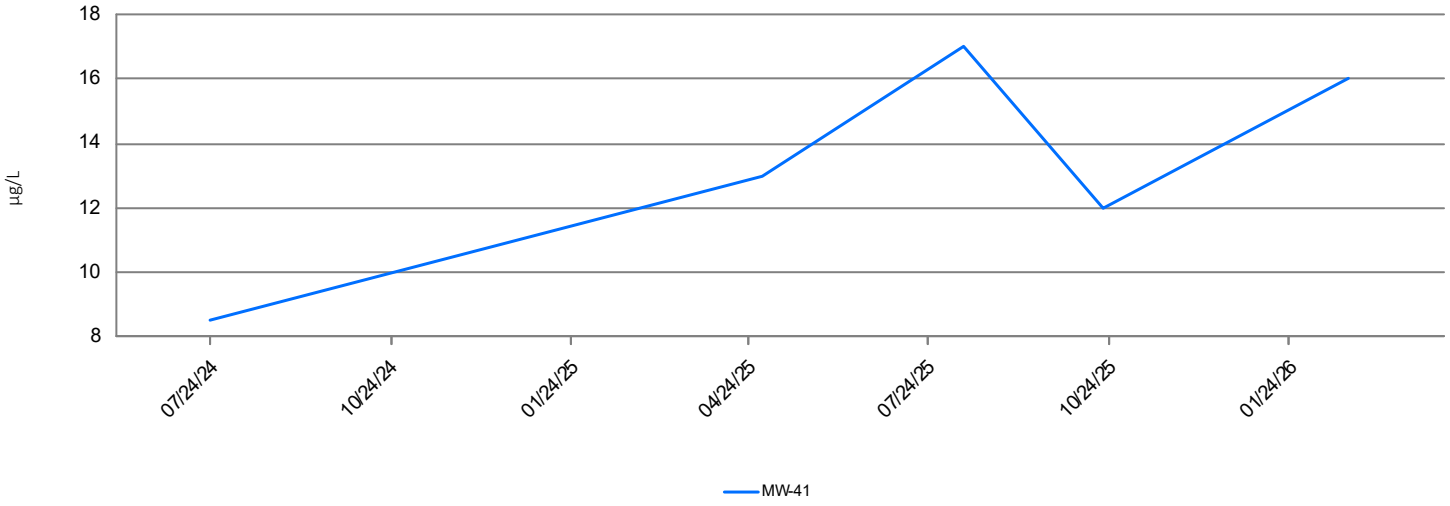
MonitorPro

No Group Selected, Uranium, Dissolved (µg/L)

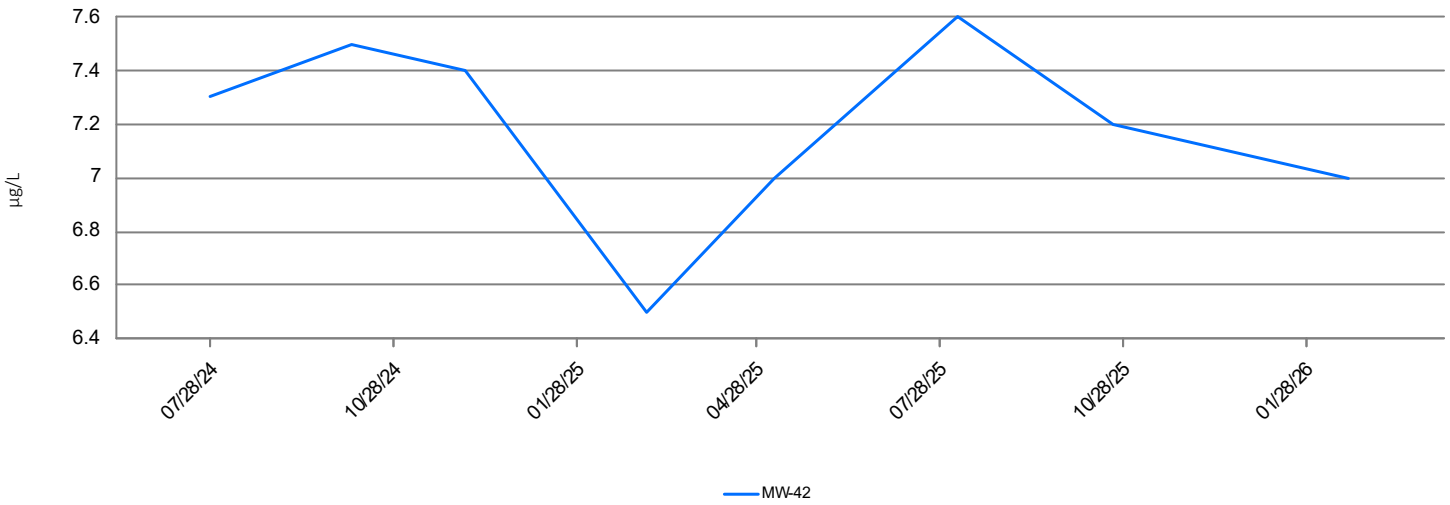
MW-3B



MW-41



MW-42

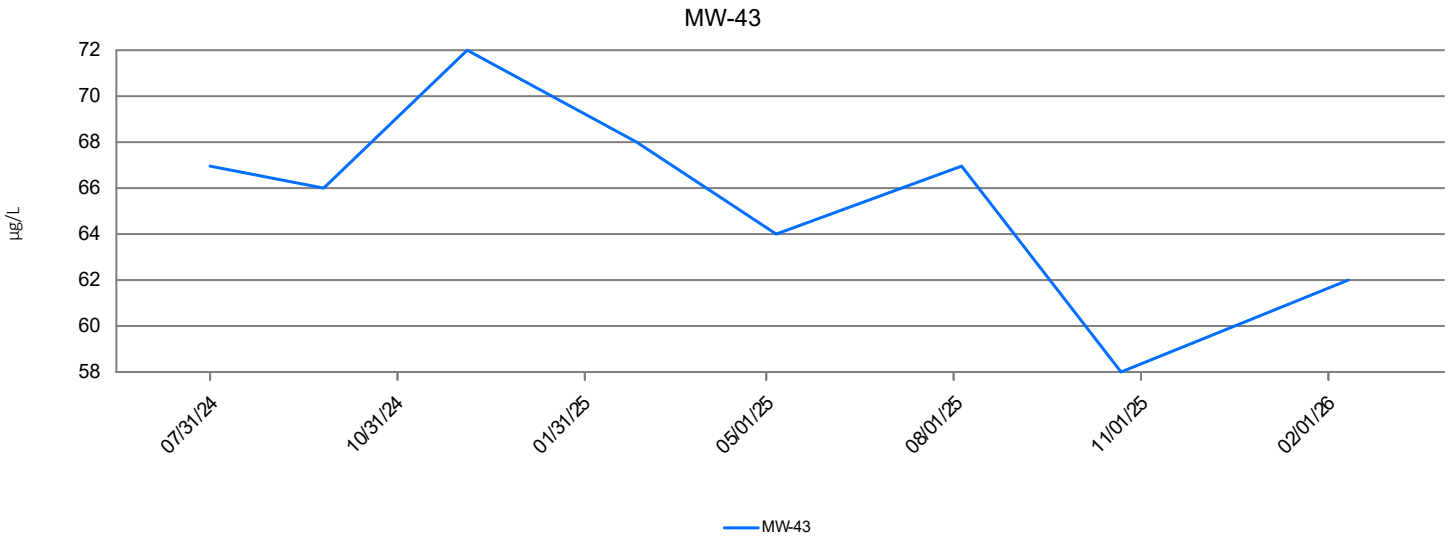


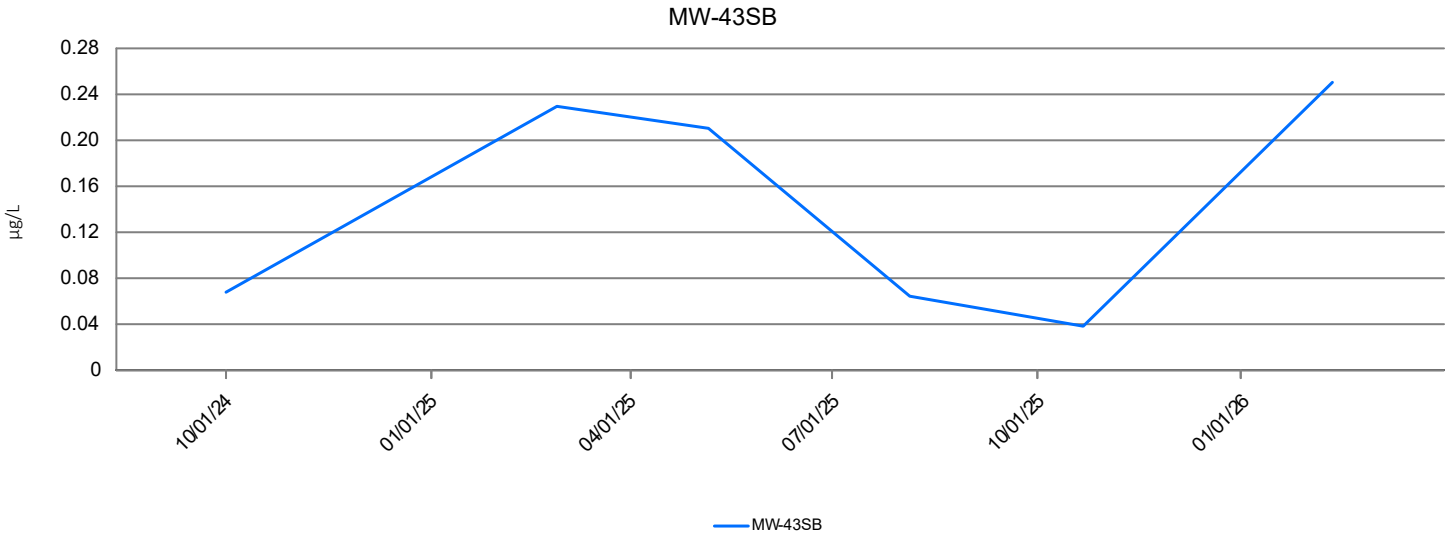
Variable Graphical Report

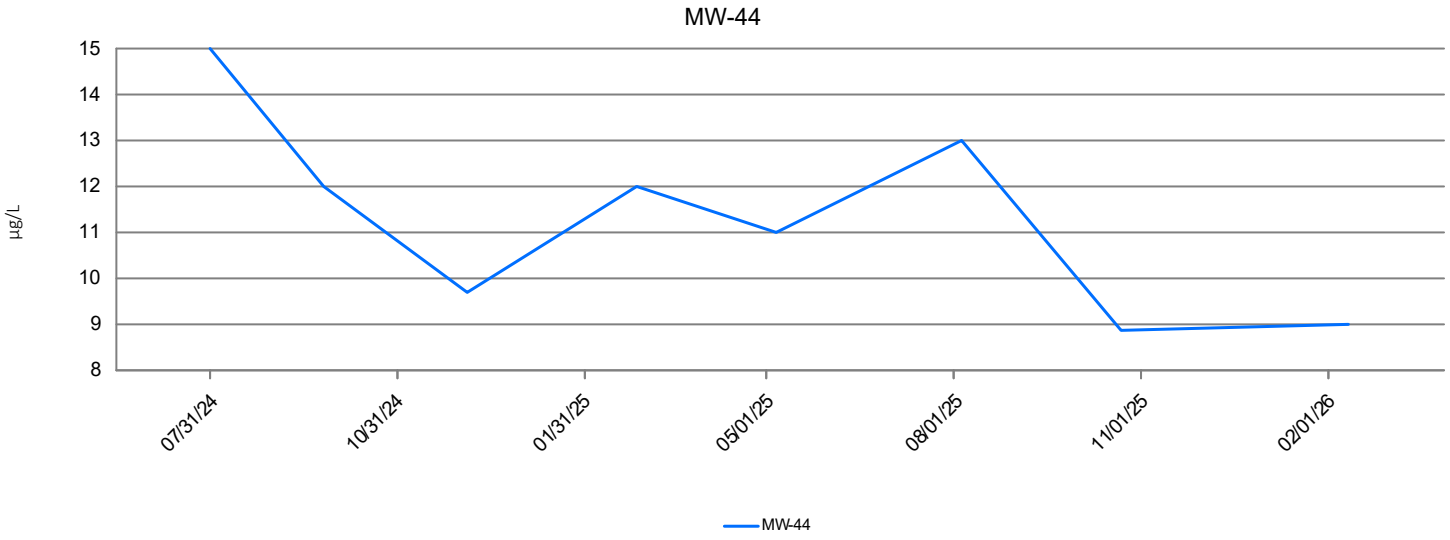
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Uranium, Dissolved (µg/L)







Printed Date: 05/21/2026

EHS DATA

MCERTS Cert. no. Sira MC090140/02

MCERTS

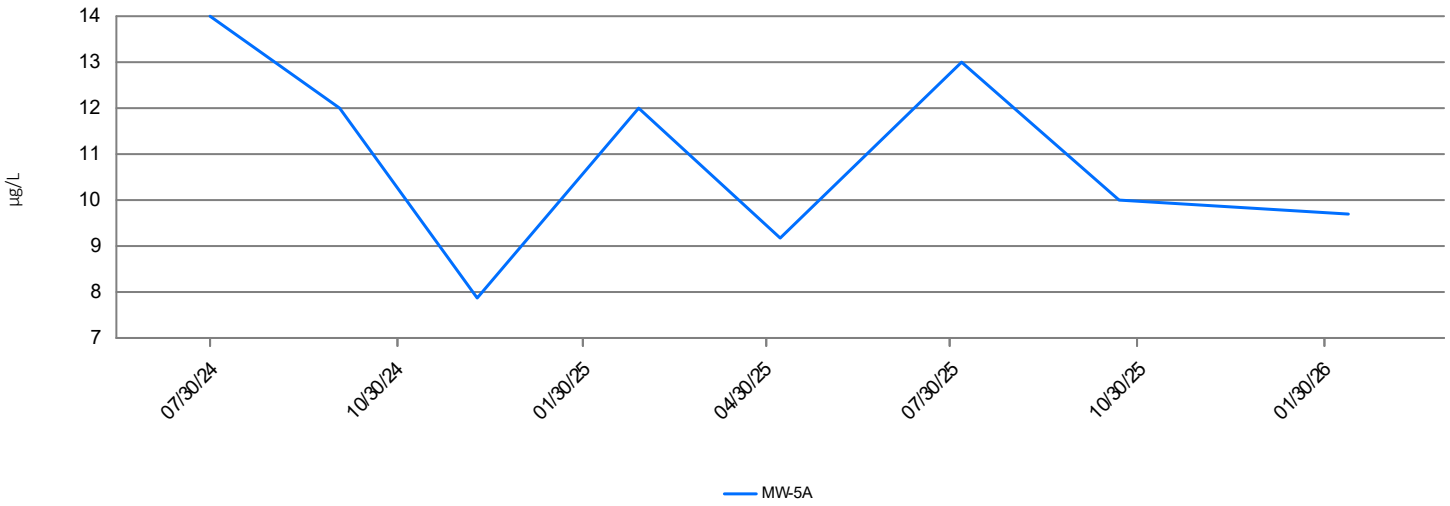
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

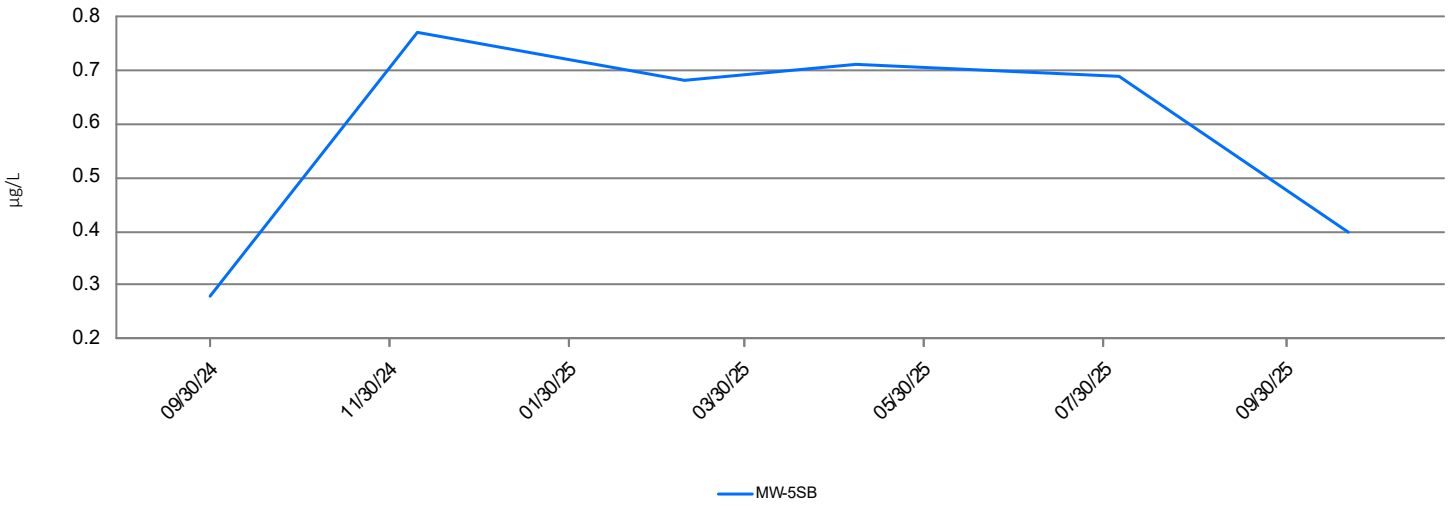
MonitorPro

No Group Selected, Uranium, Dissolved (µg/L)

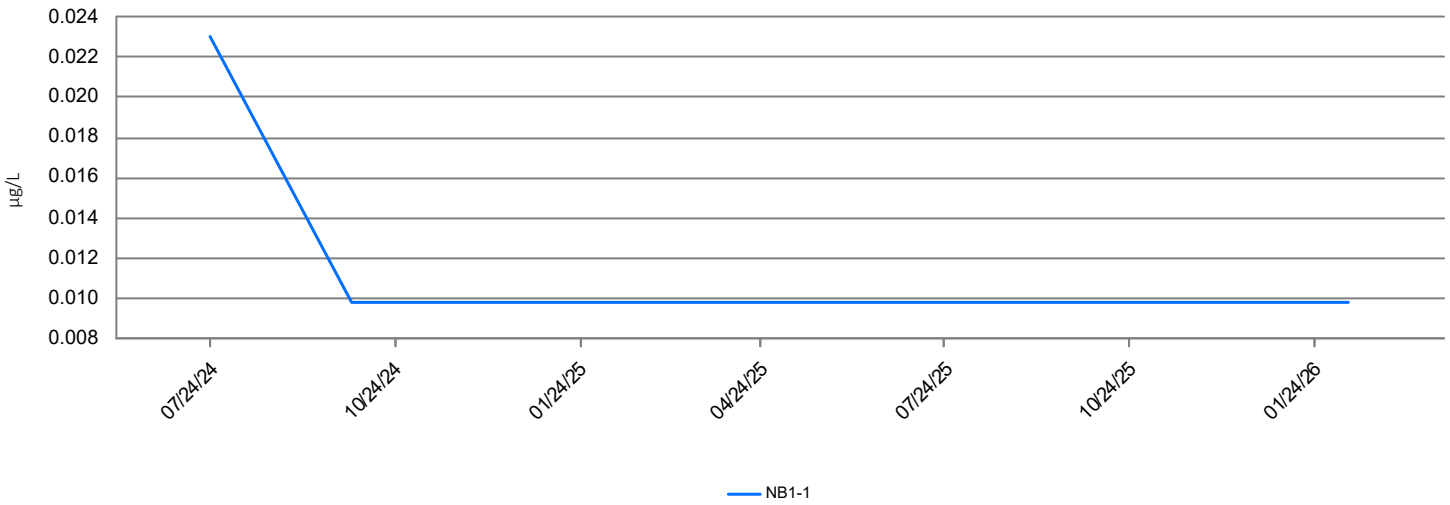
MW-5A



MW-5SB



NB1-1



Printed Date: 05/21/2026

EHS DATA

MCERTS Cert. no. Sira MC090140/02

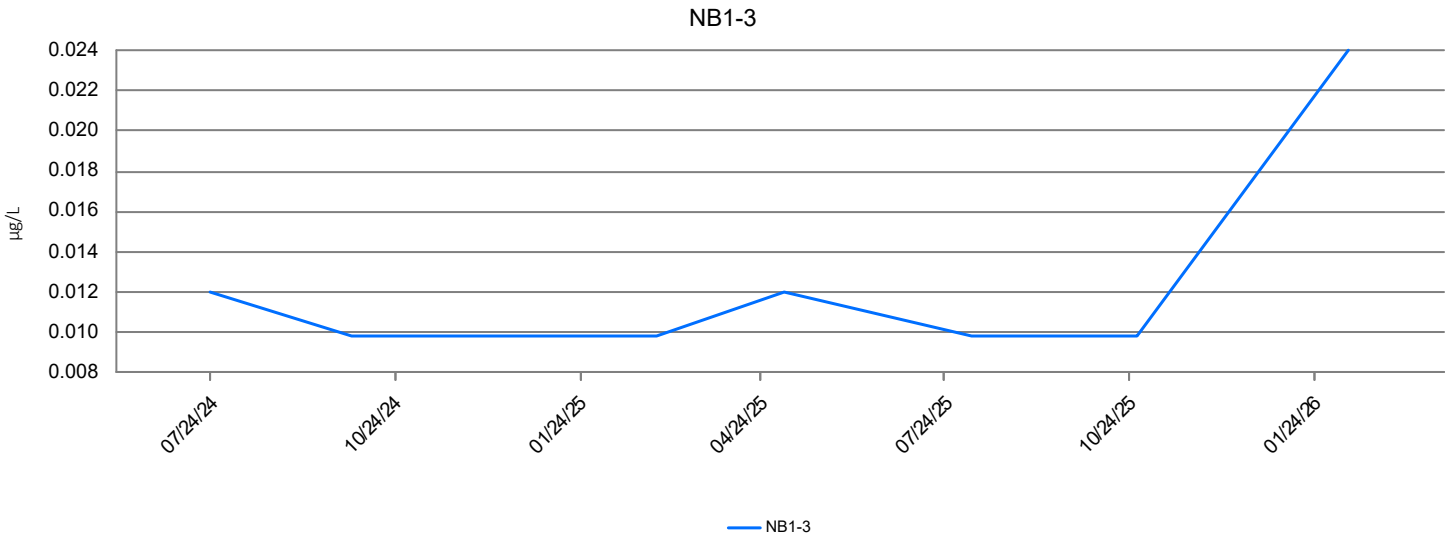
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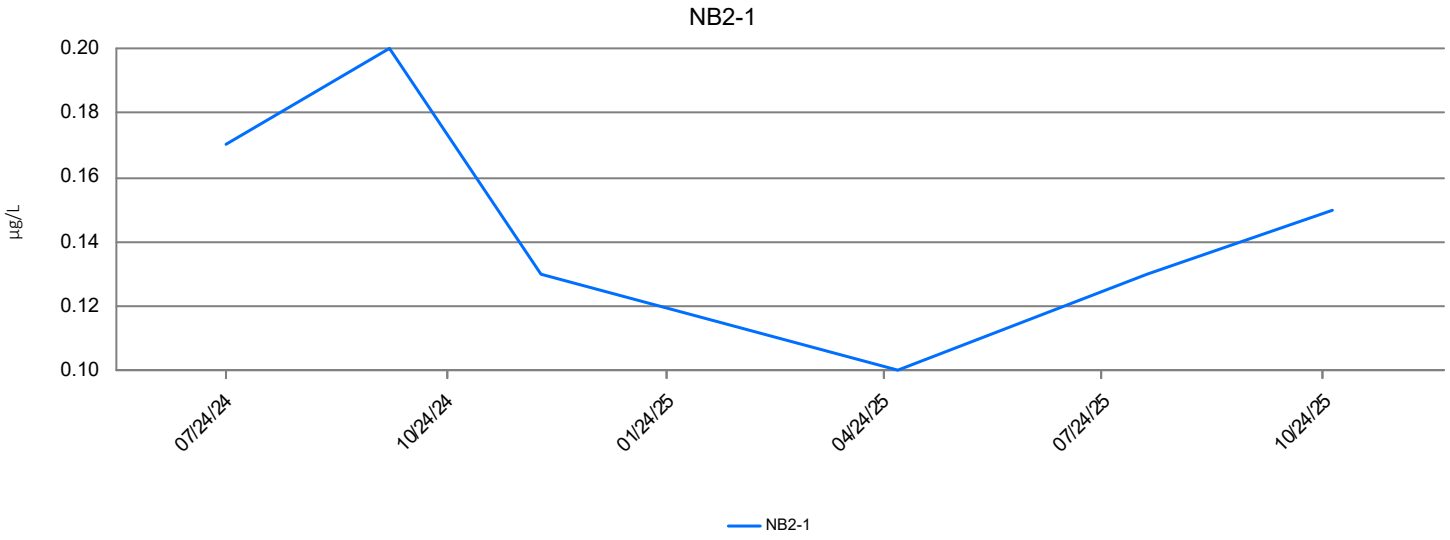
Variable Graphical Report

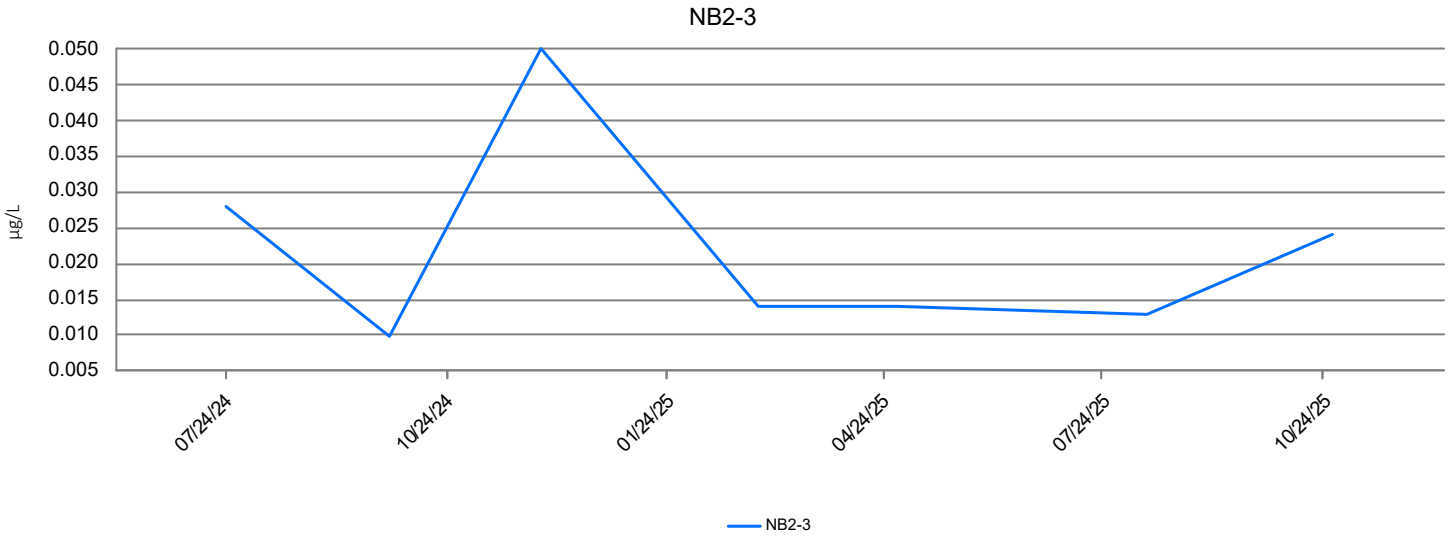
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Uranium, Dissolved (µg/L)







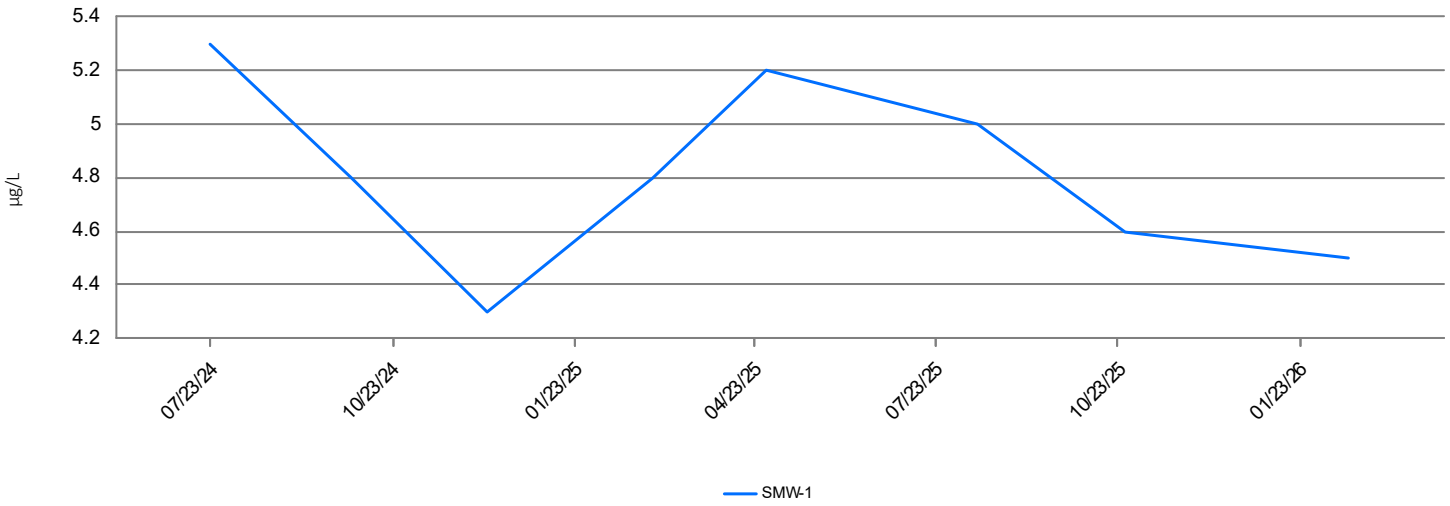
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

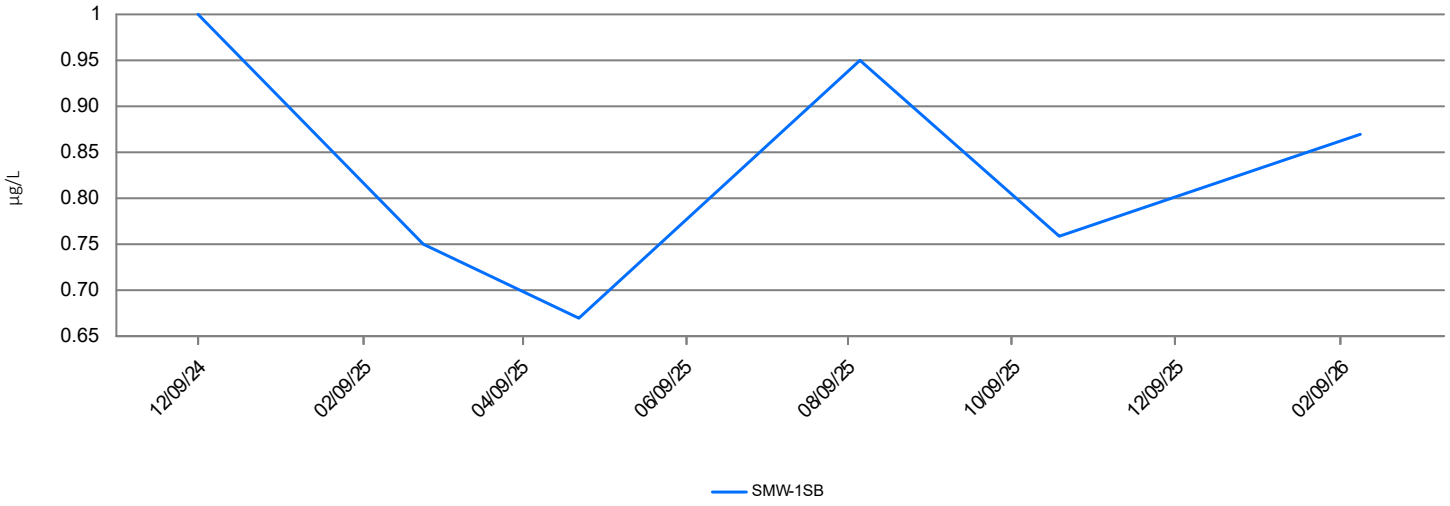
MonitorPro

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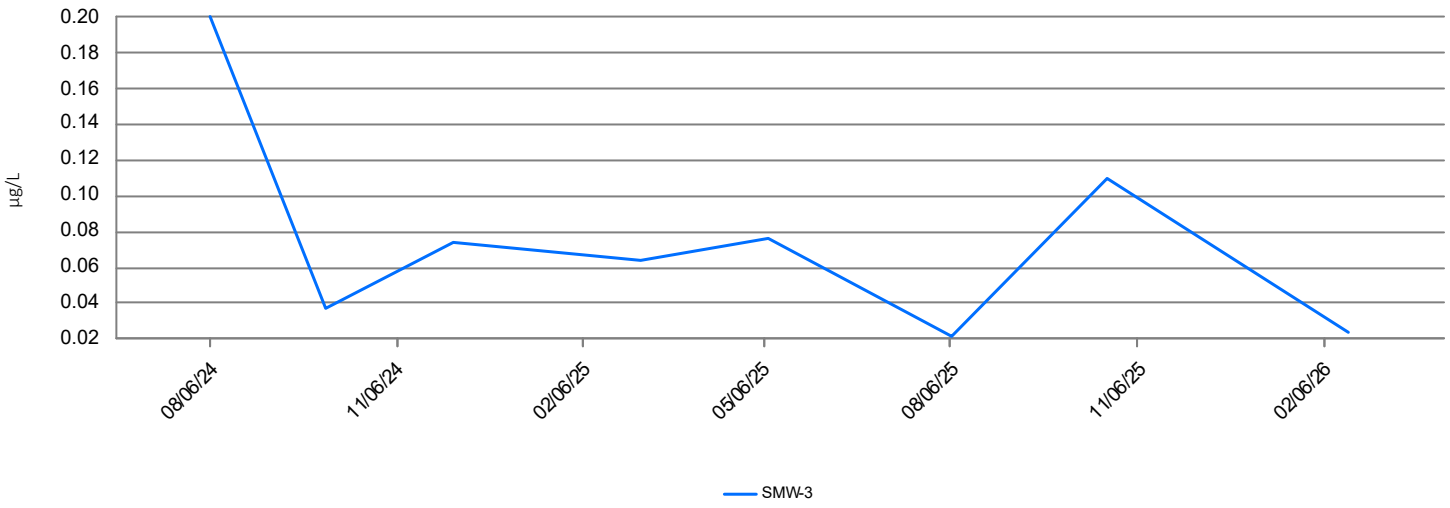
SMW-1



SMW-1SB



SMW-3

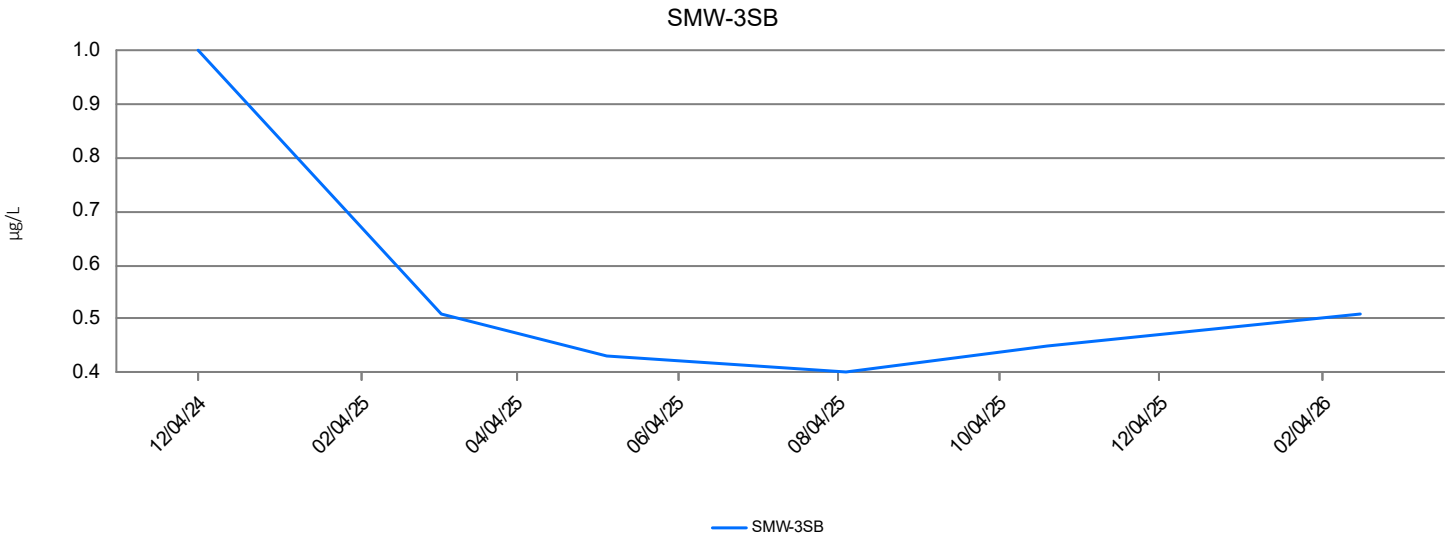


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Uranium, Dissolved (µg/L)

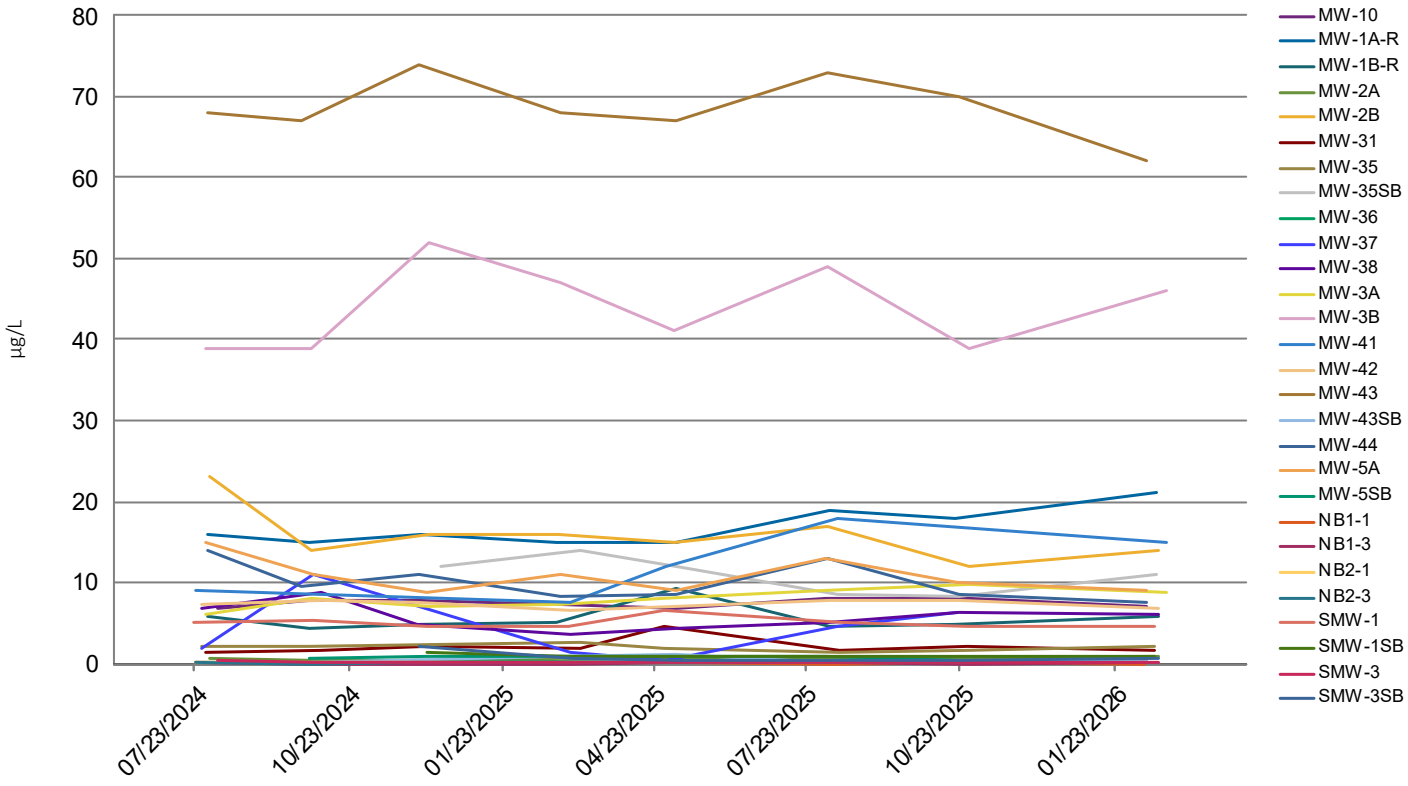


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Uranium, Total Recoverable (µg/L)



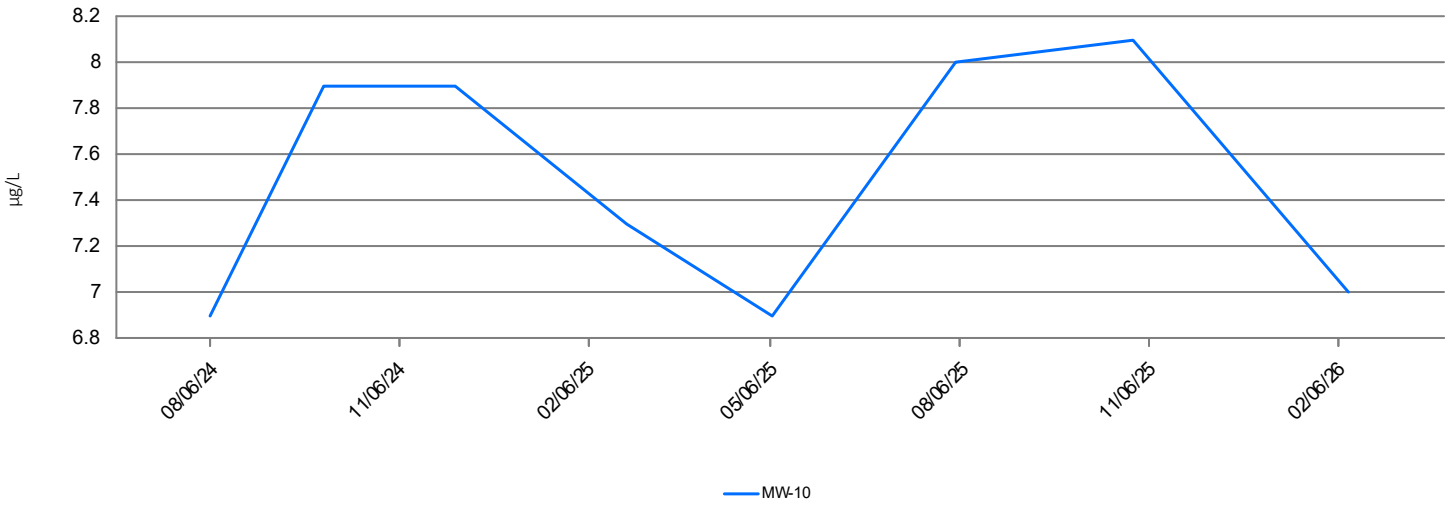
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

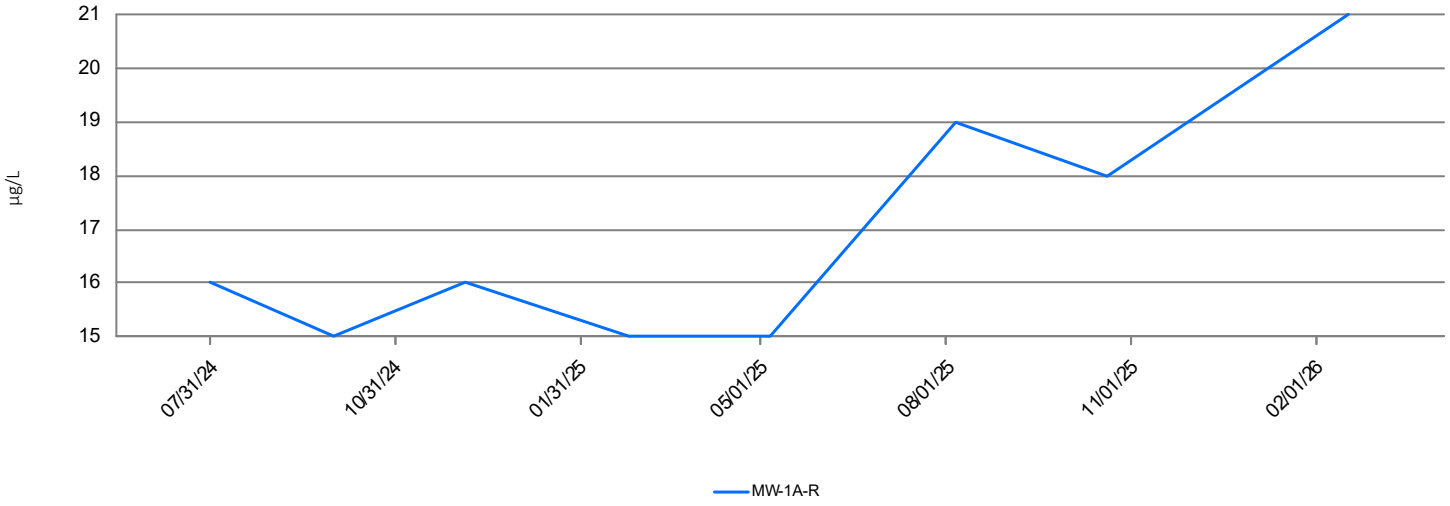
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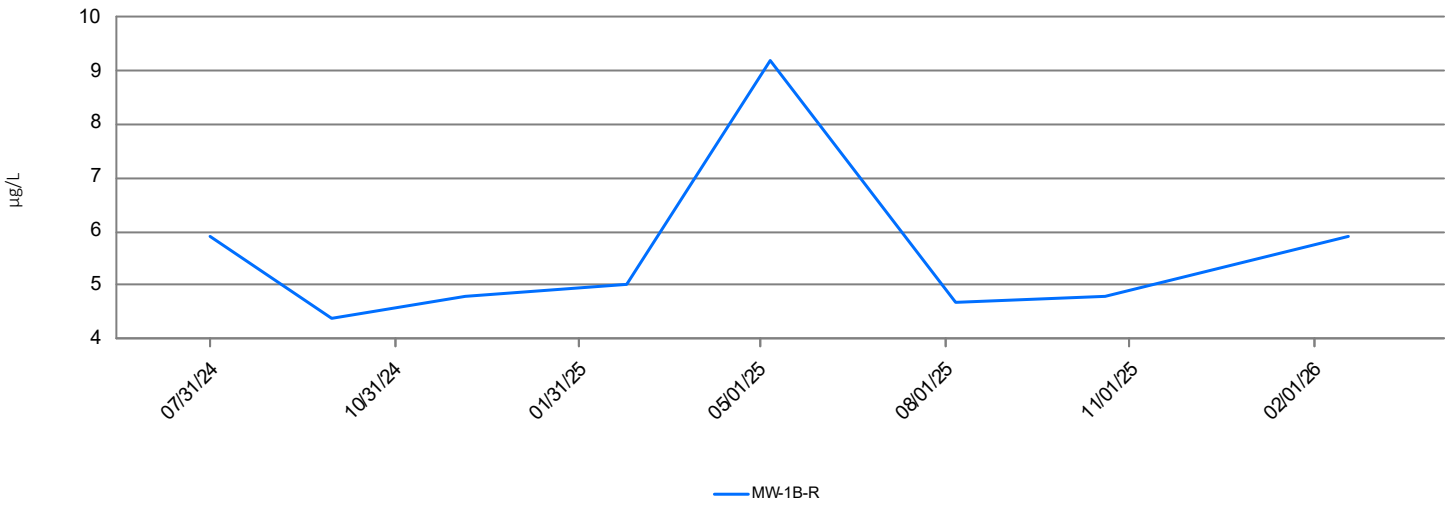
MW-10



MW-1A-R



MW-1B-R



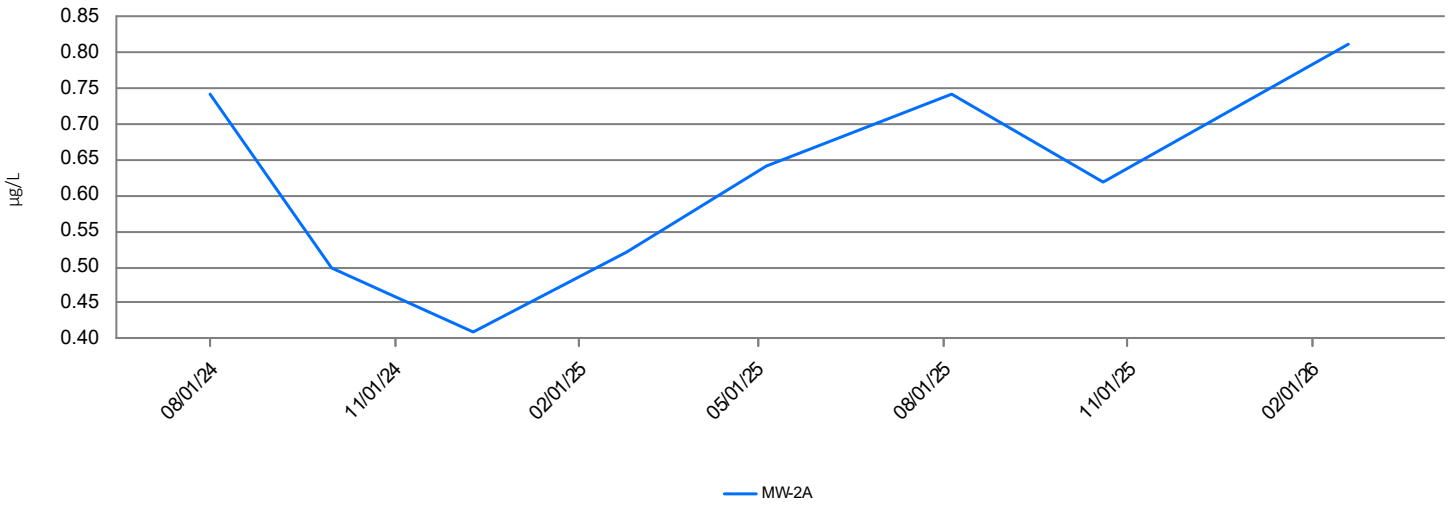
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

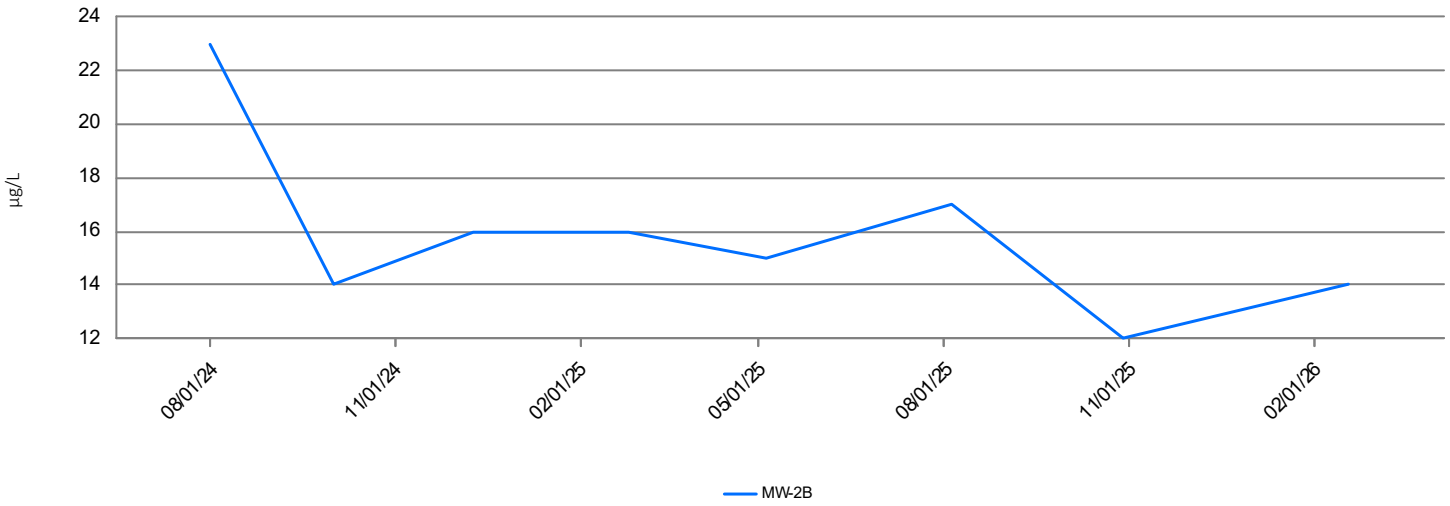
MonitorPro

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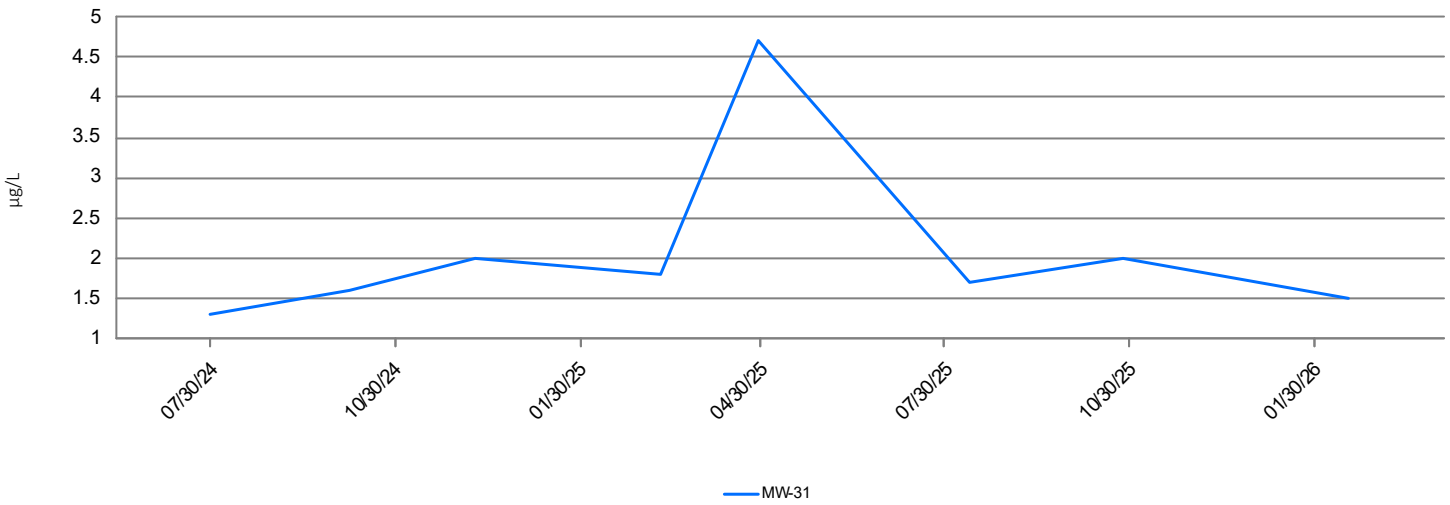
MW-2A



MW-2B



MW-31

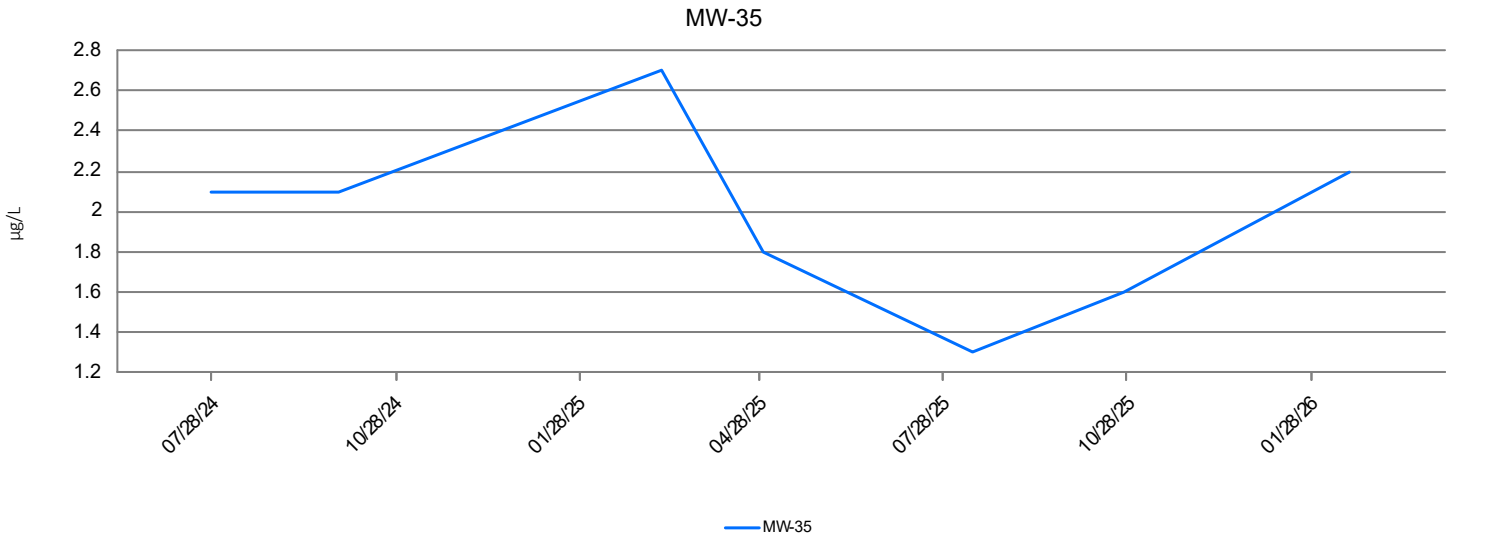


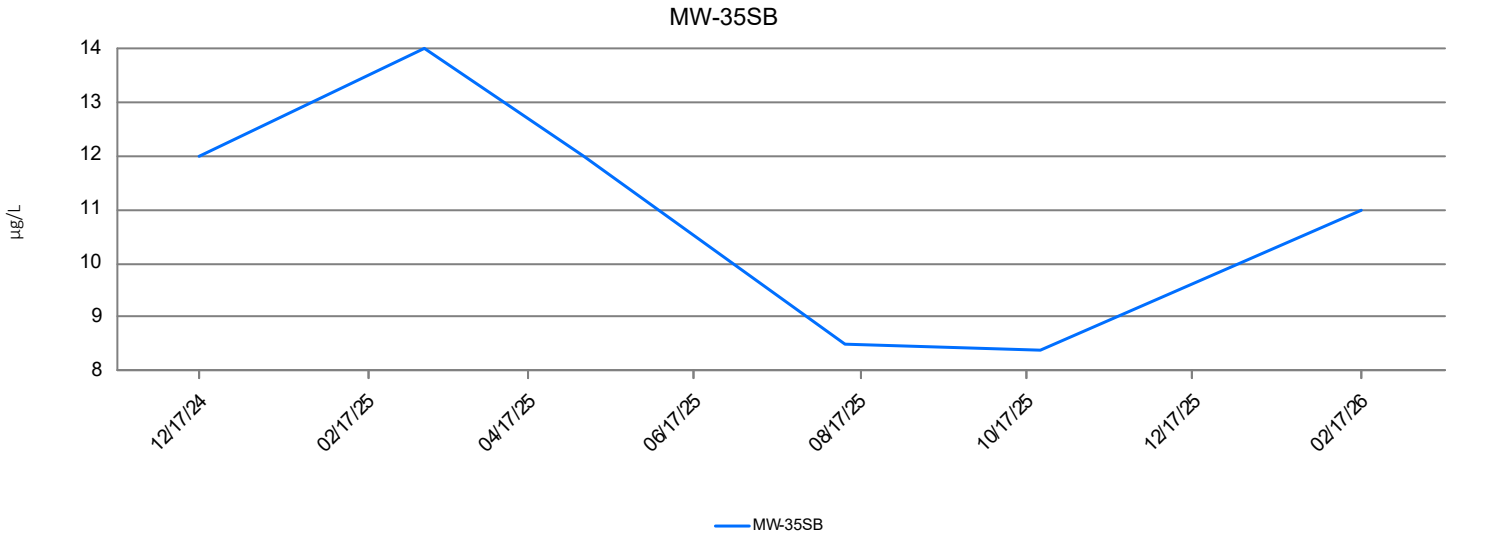
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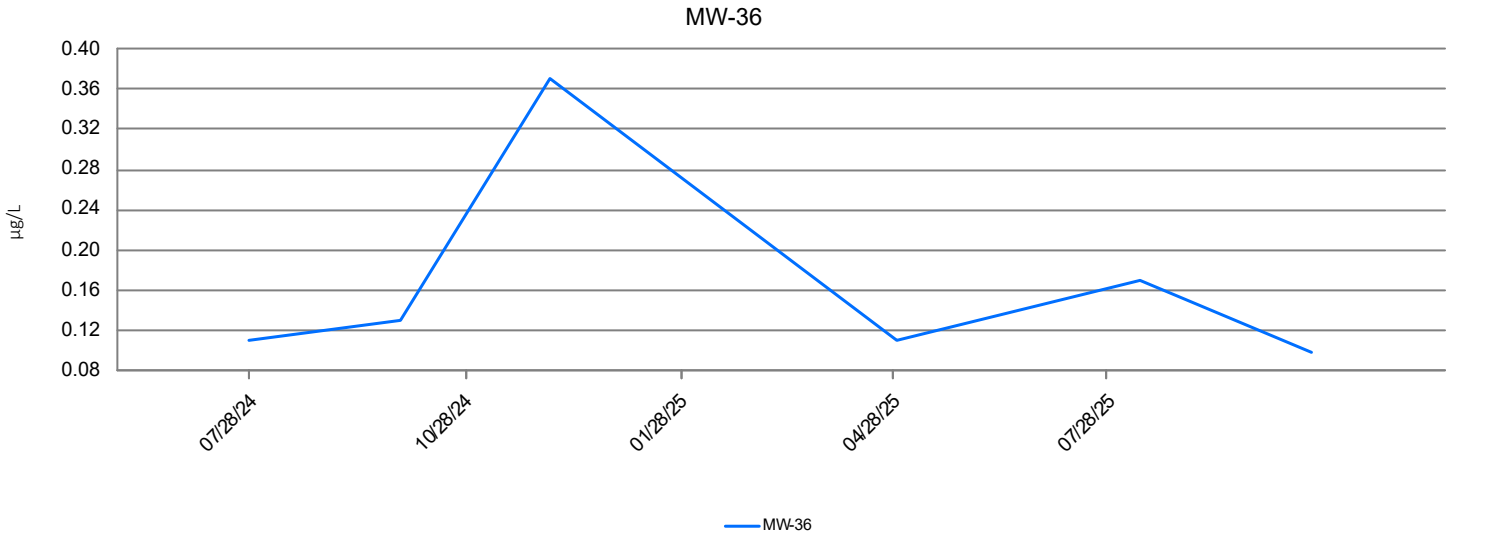
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Uranium, Total Recoverable (µg/L)





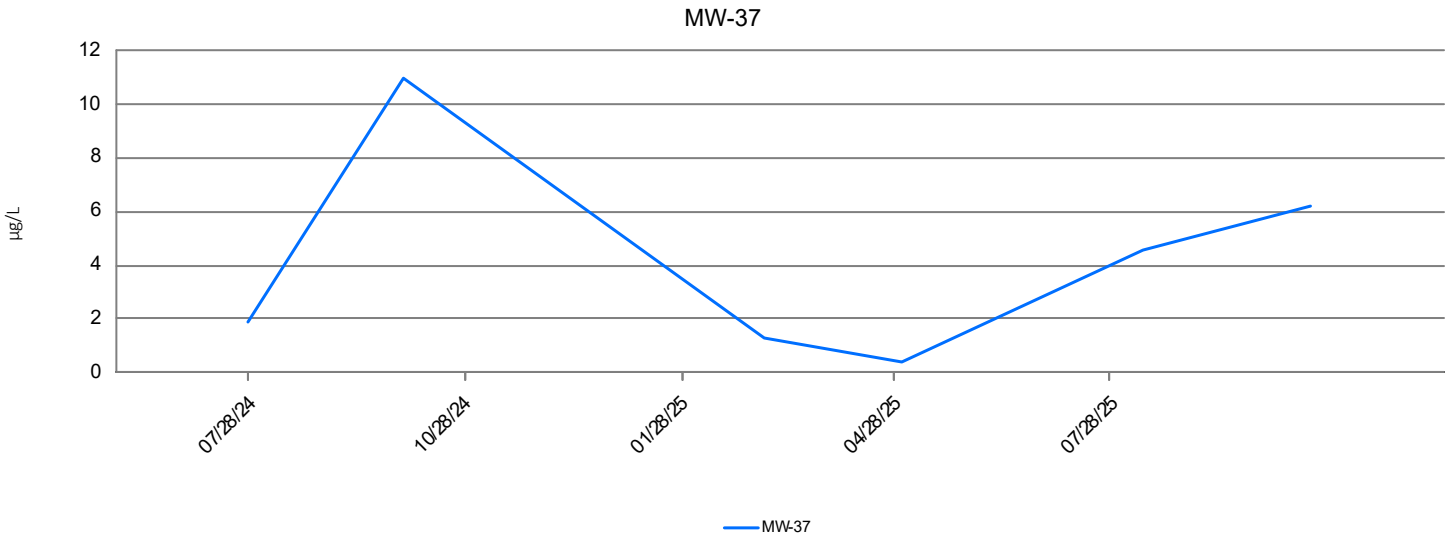


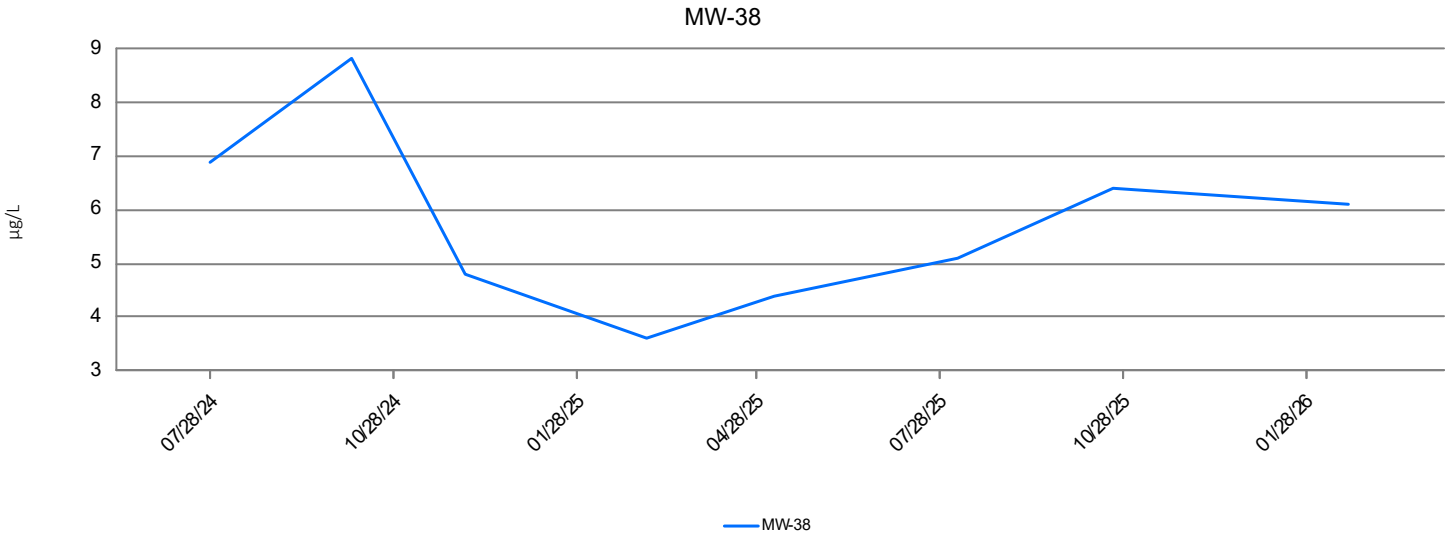
Variable Graphical Report

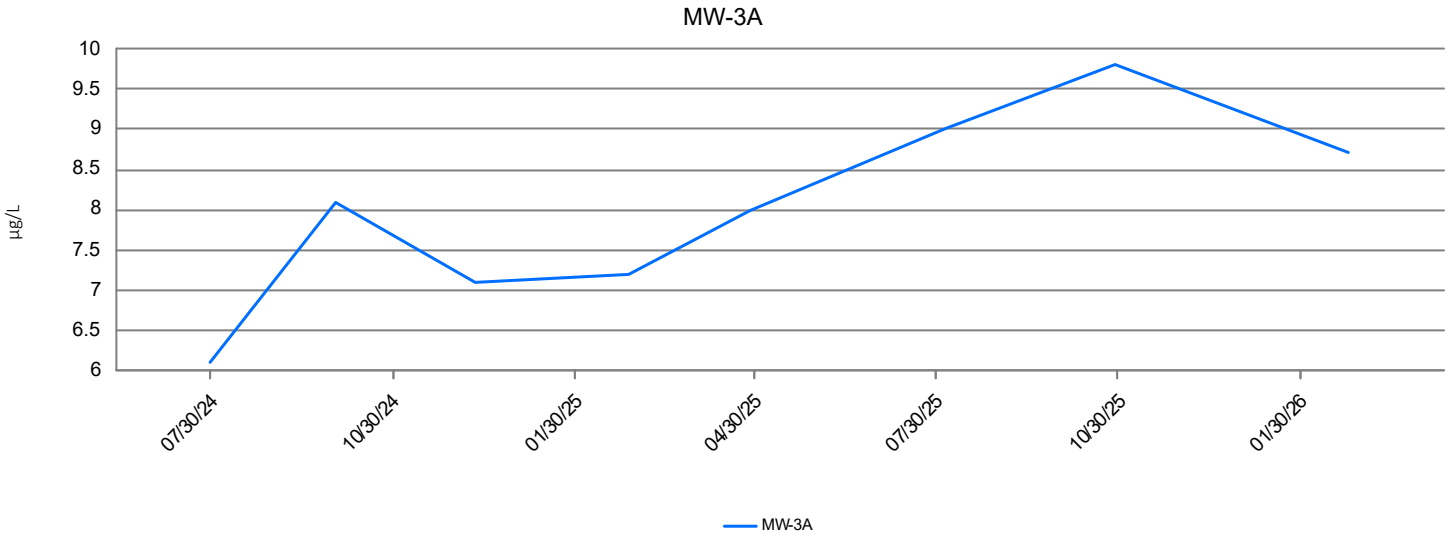
Date from 07/01/2024 to 05/01/2026

MonitorPro

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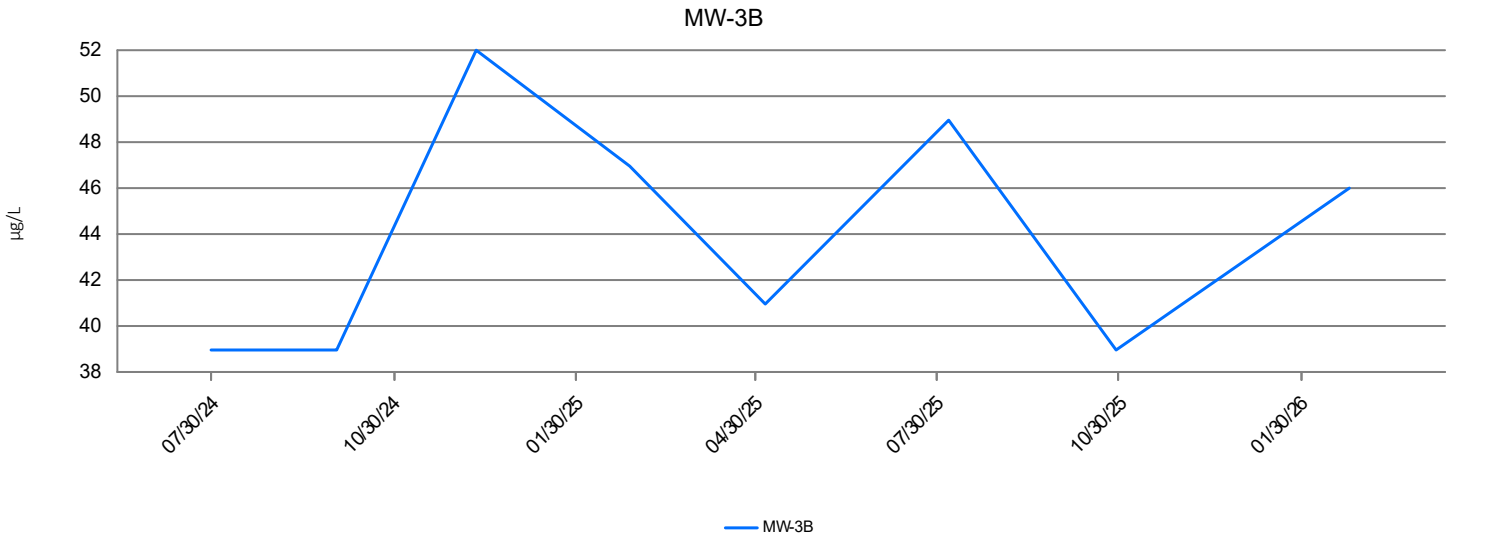


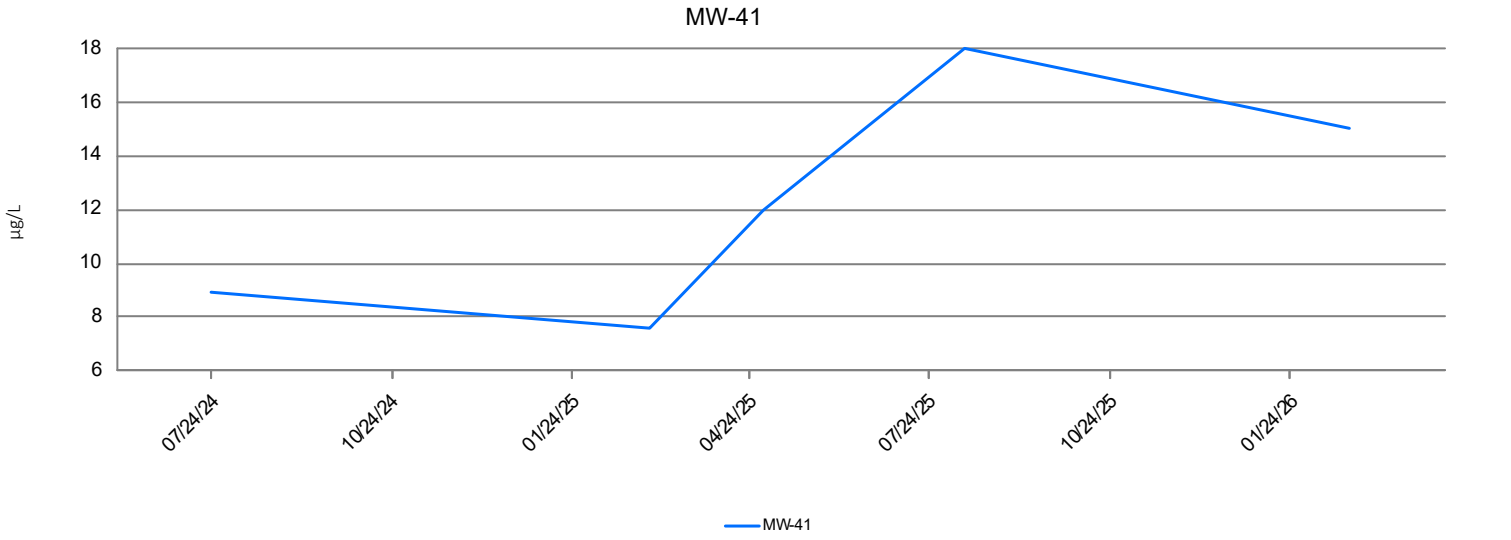
Variable Graphical Report

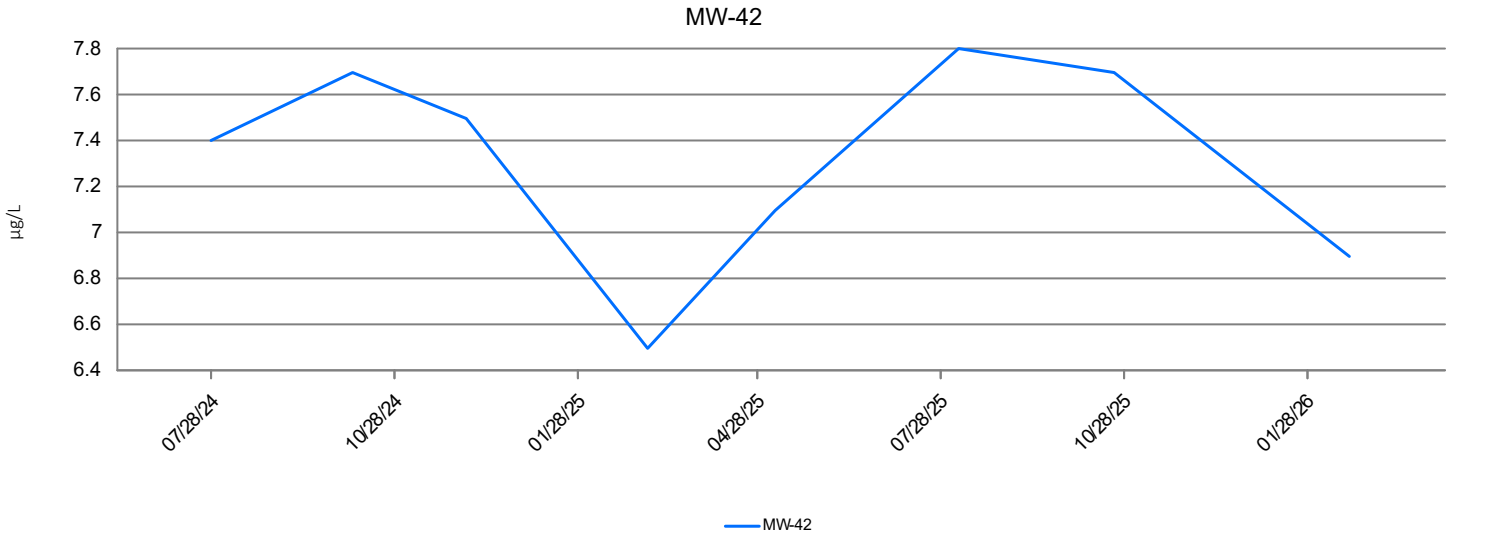
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Uranium, Total Recoverable (µg/L)





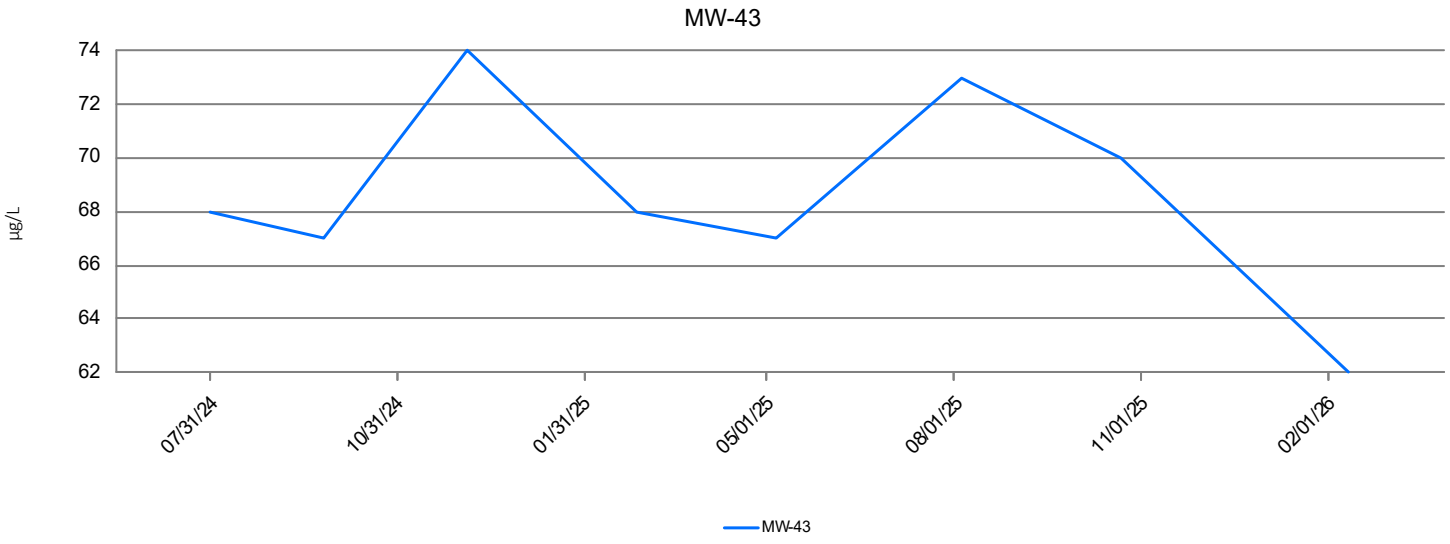


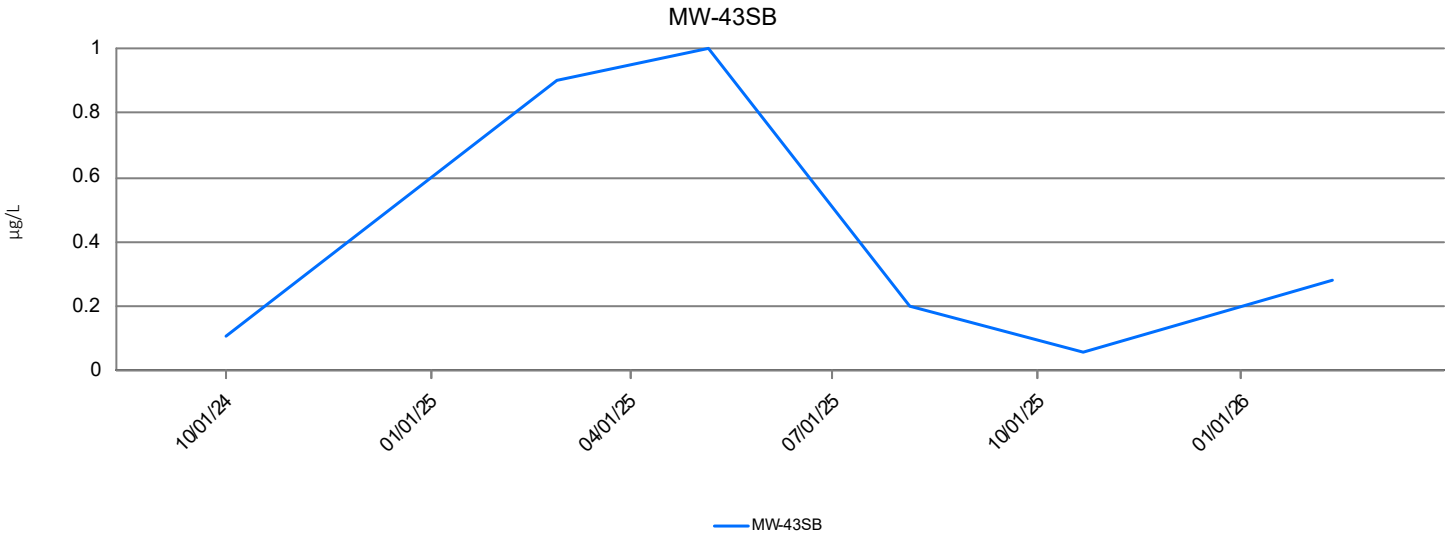
Variable Graphical Report

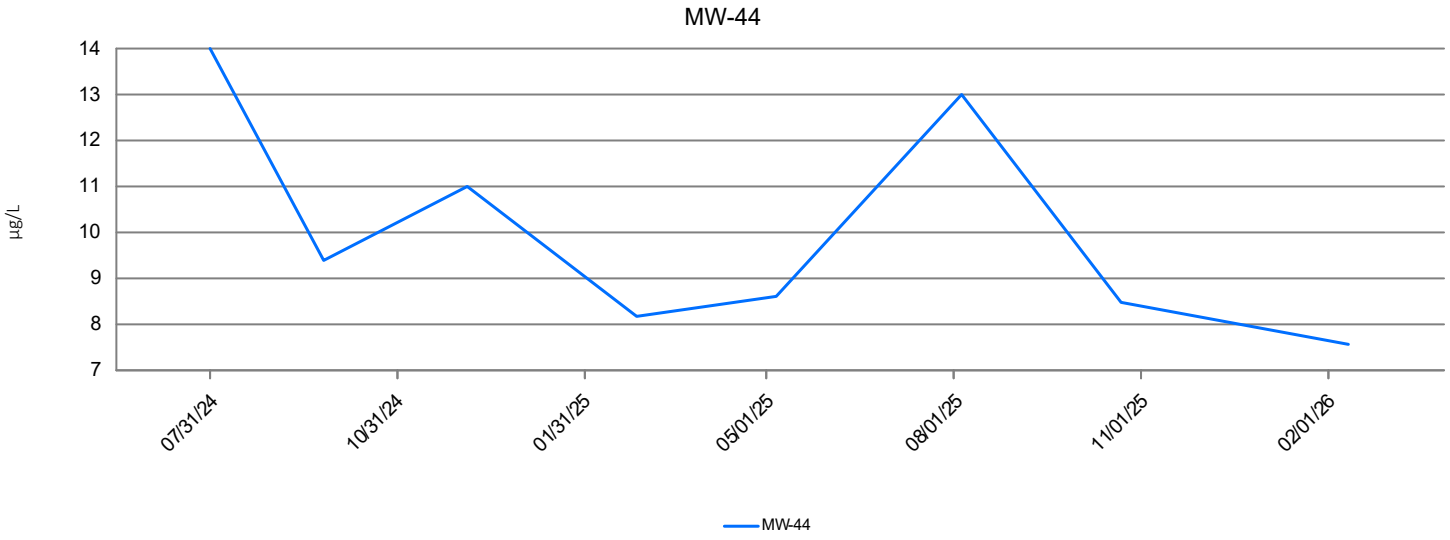
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Uranium, Total Recoverable (µg/L)





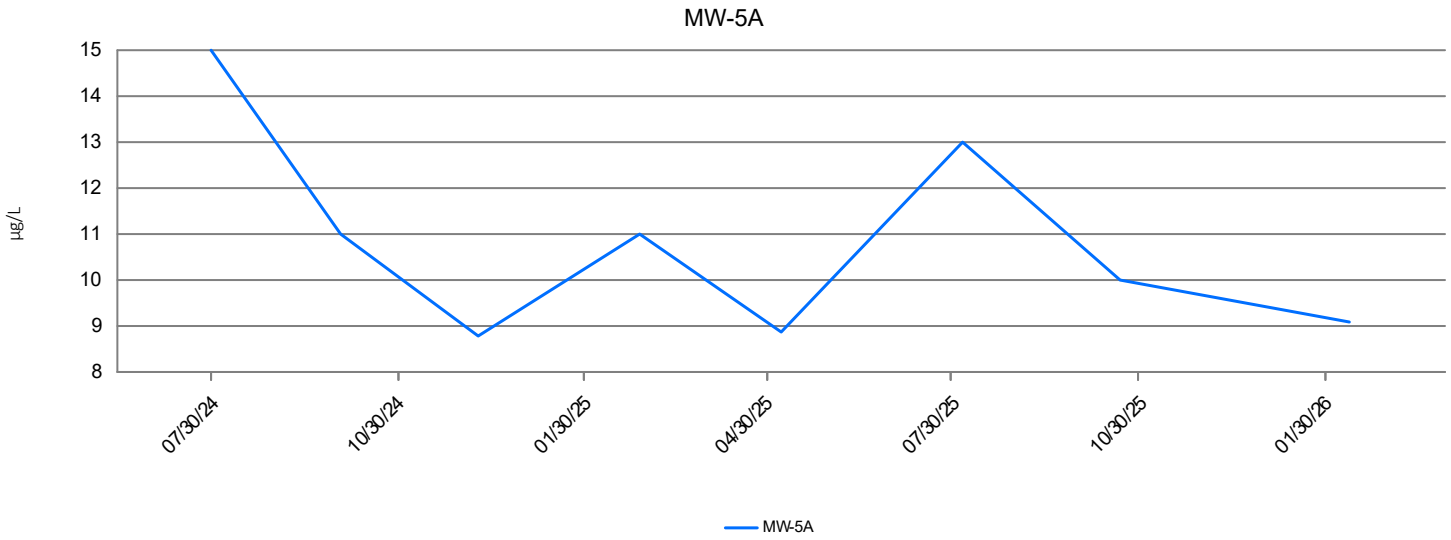


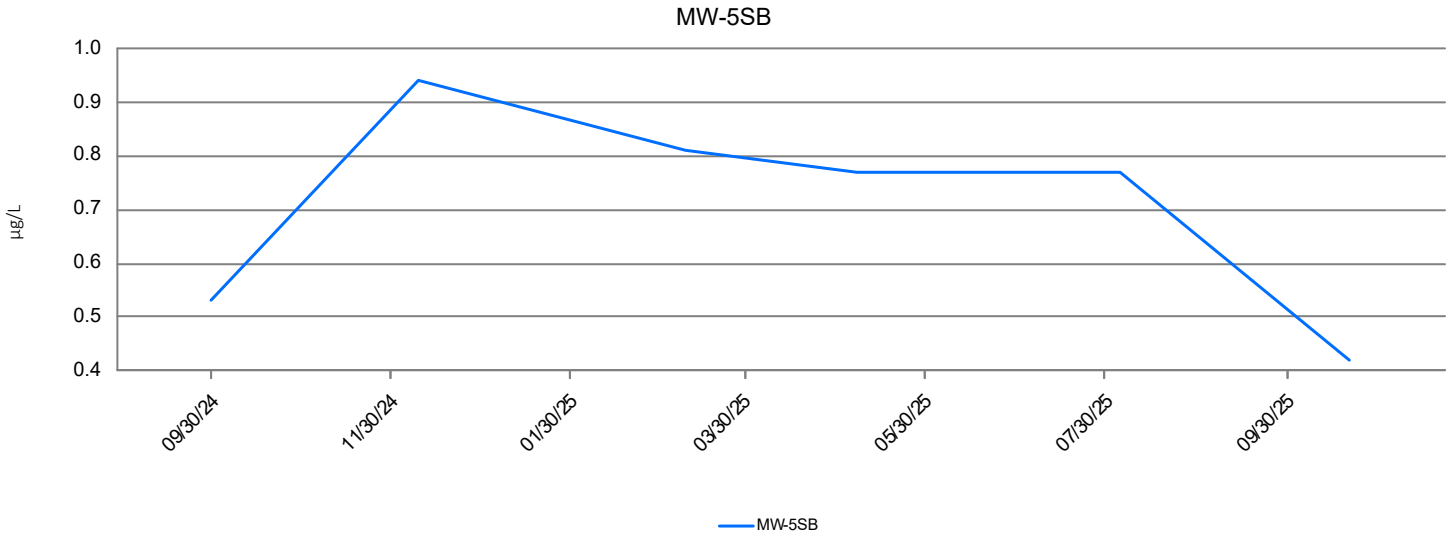
Variable Graphical Report

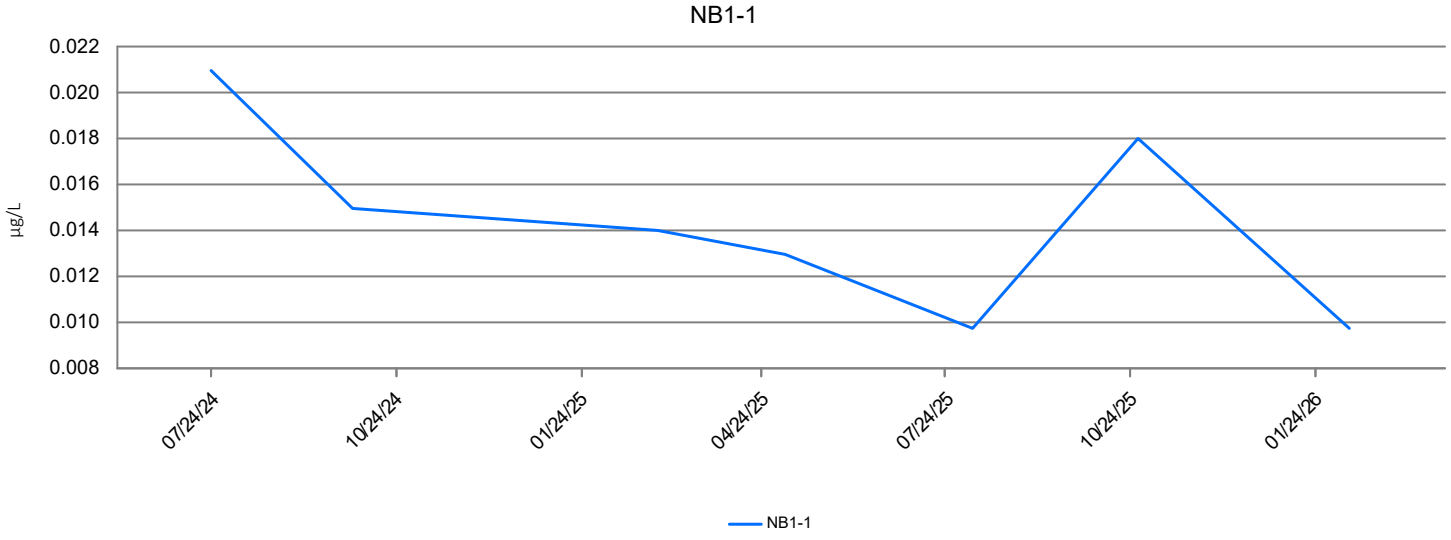
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Uranium, Total Recoverable (µg/L)







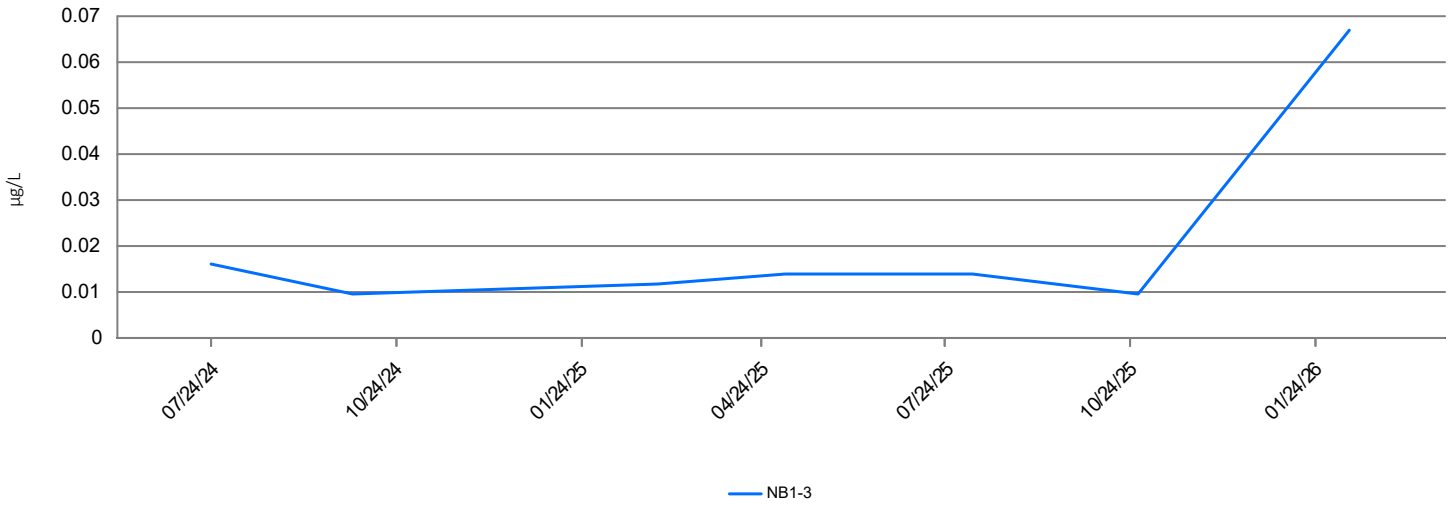
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

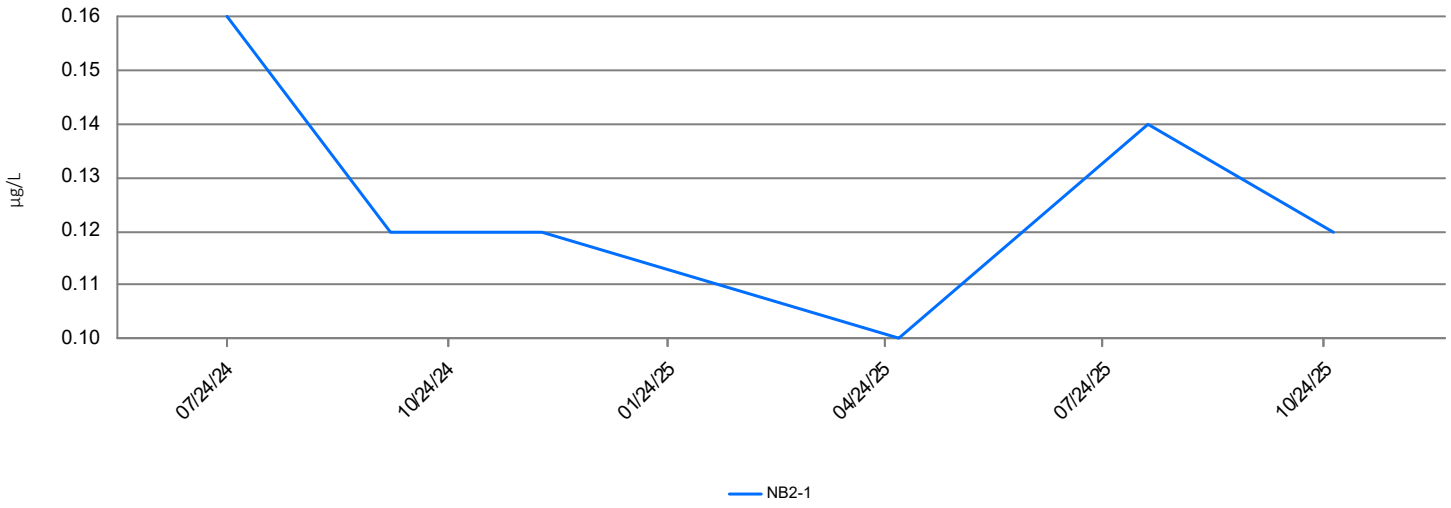
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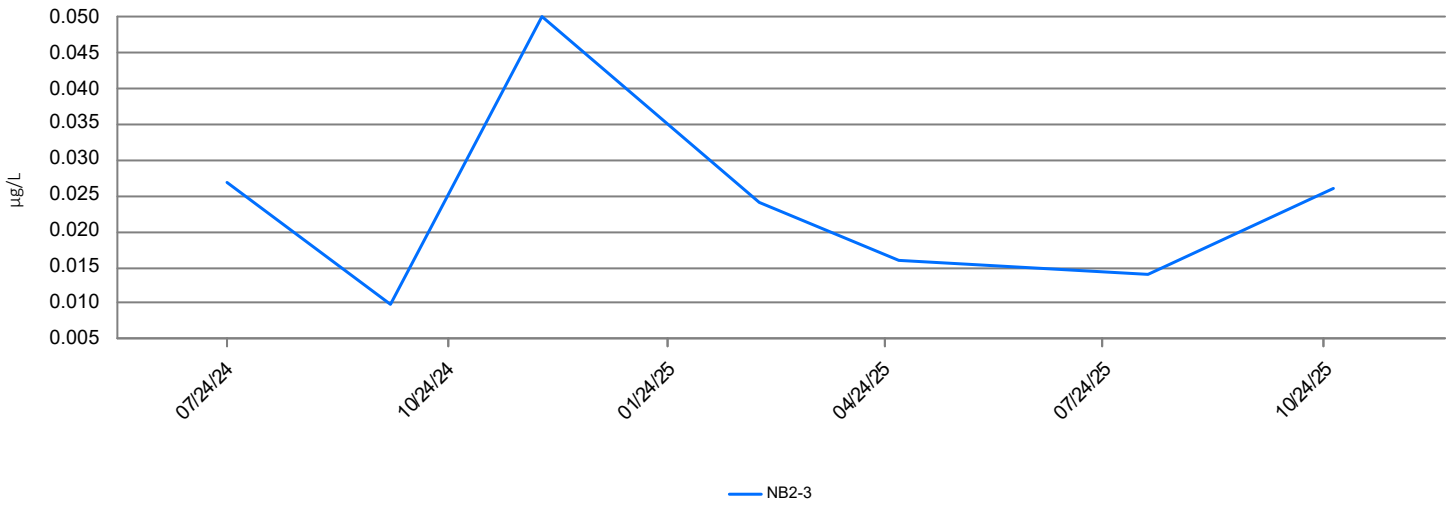
NB1-3



NB2-1



NB2-3



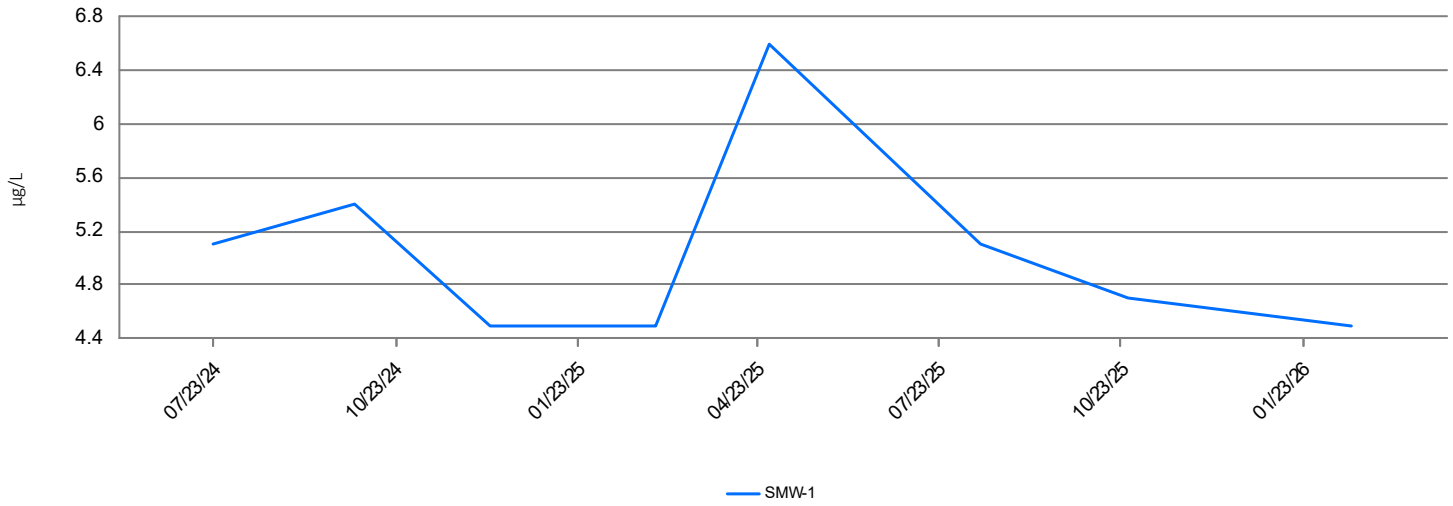
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

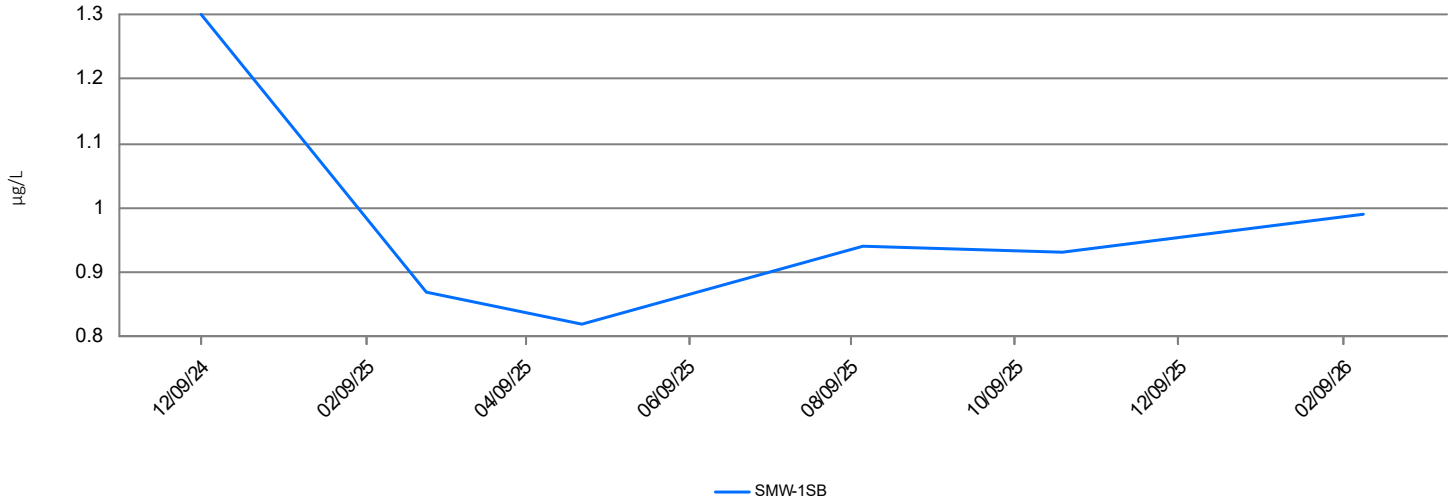
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No Group Selected, Uranium, Total Recoverable (µg/L)

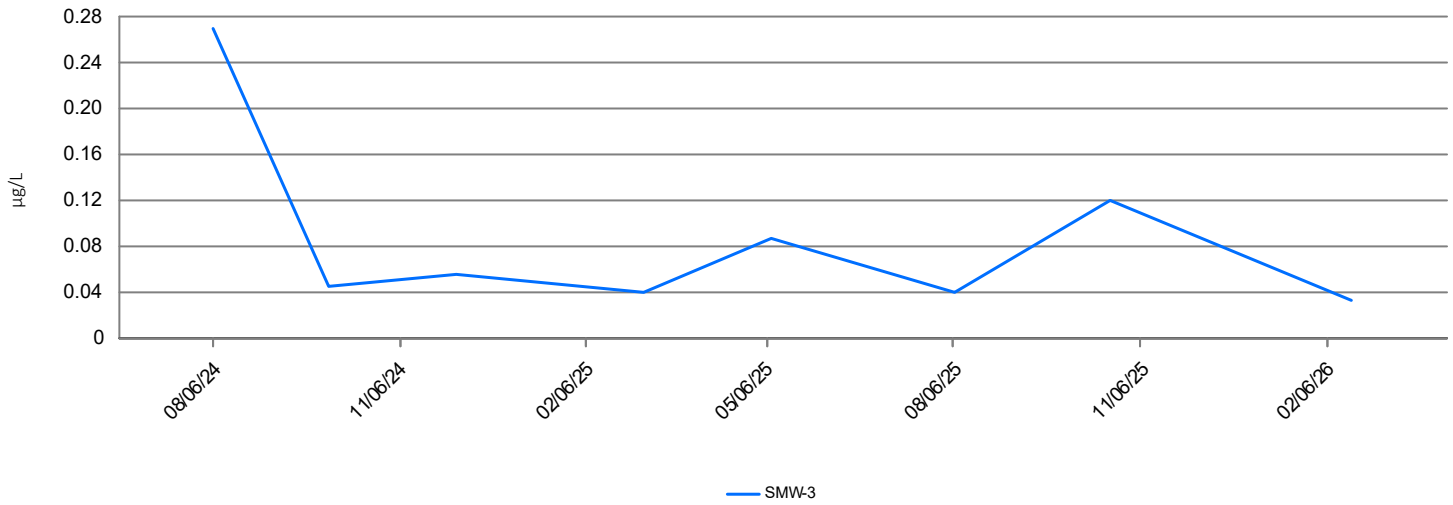
SMW-1



SMW-1SB



SMW-3

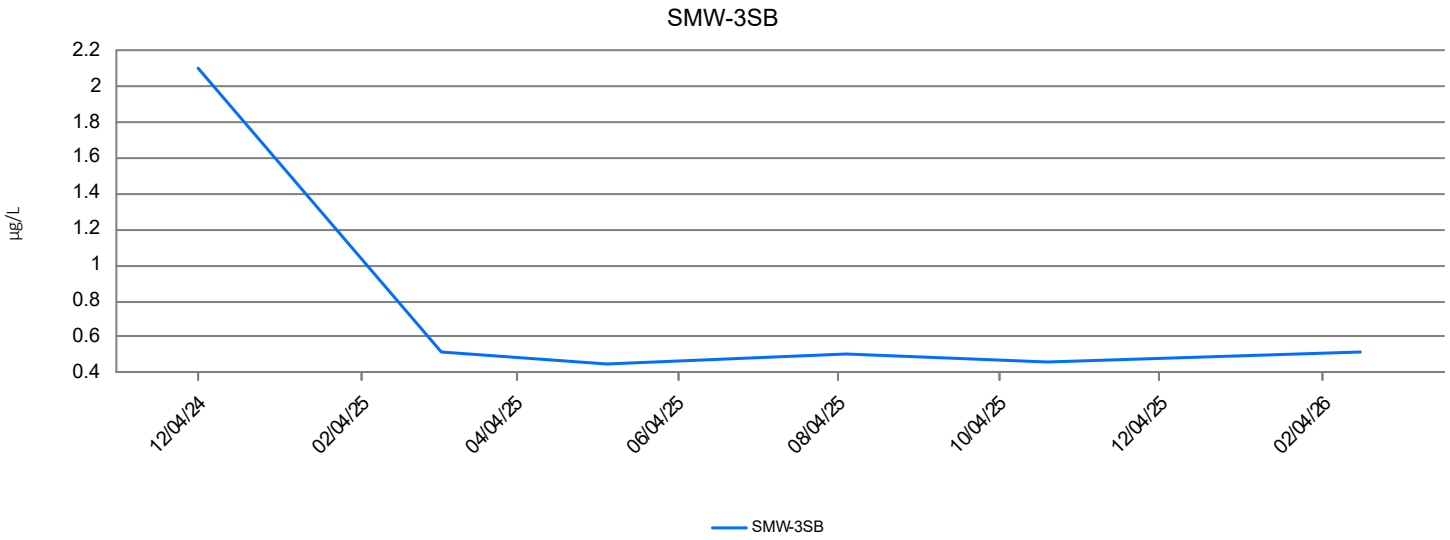


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Uranium, Total Recoverable (µg/L)

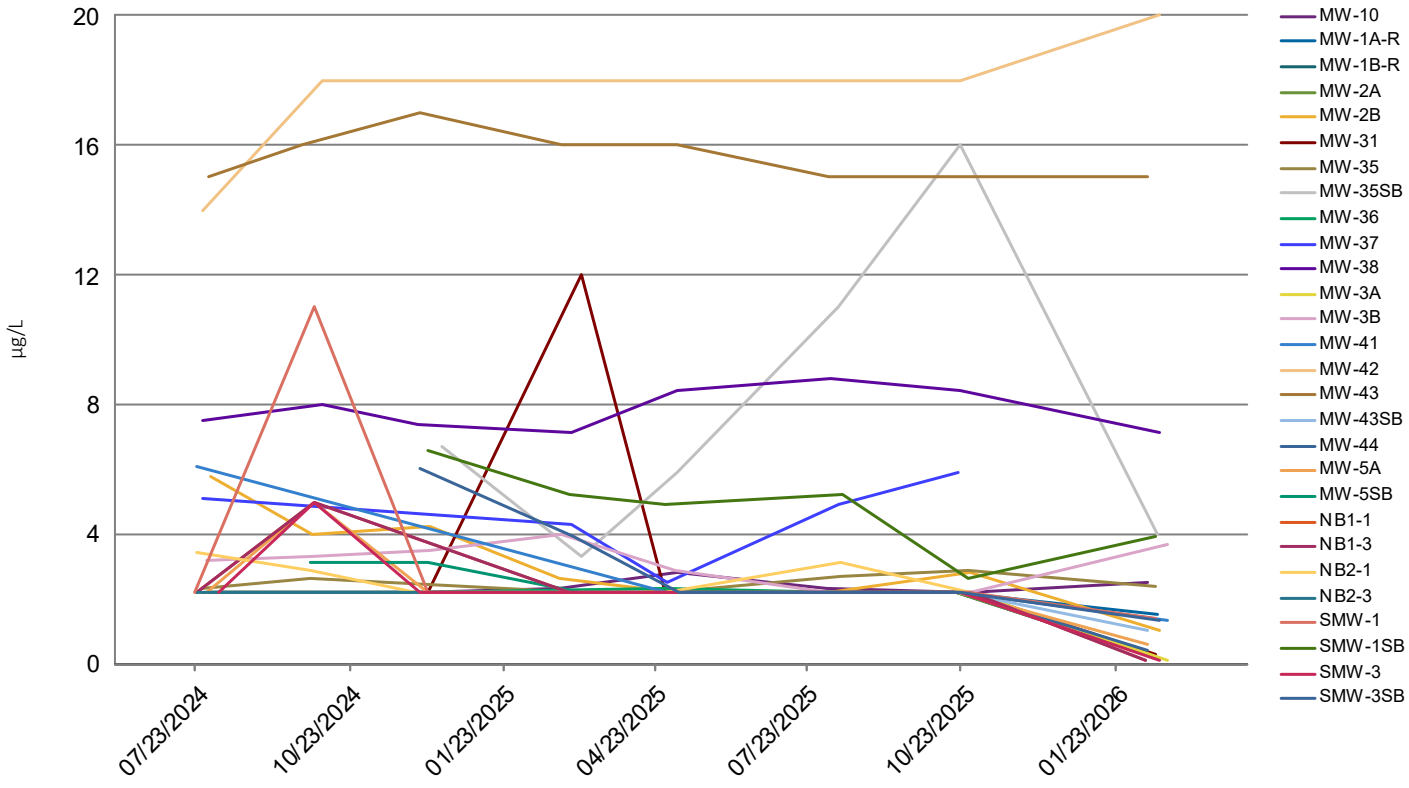


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Vanadium, Dissolved (µg/L)

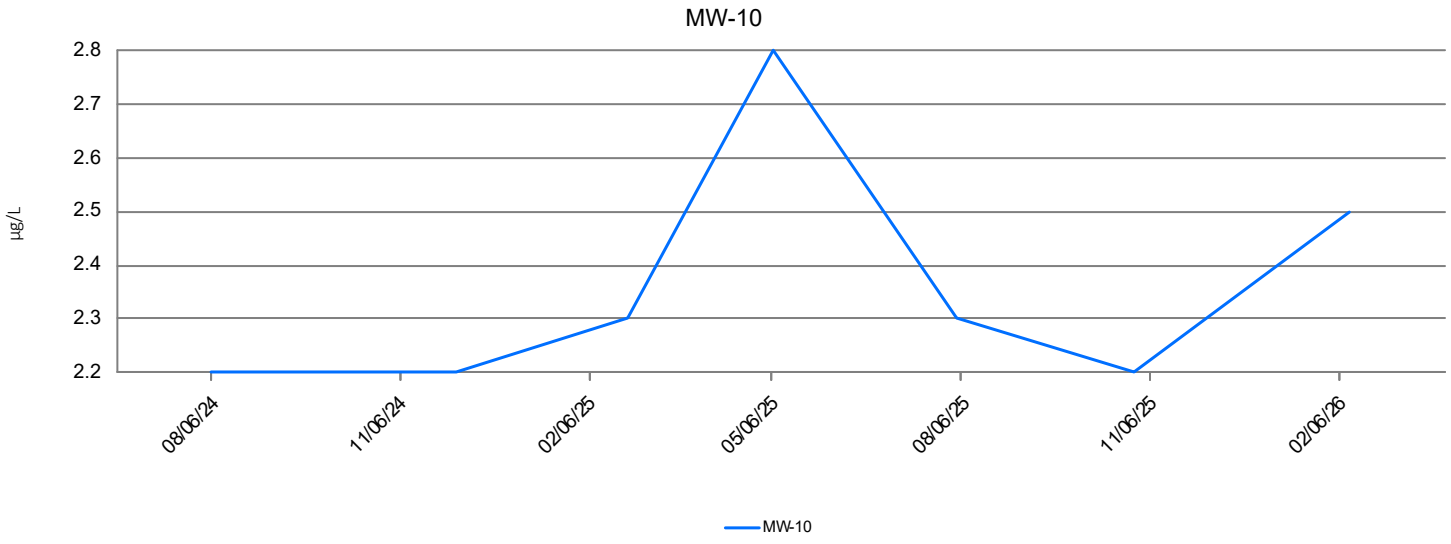


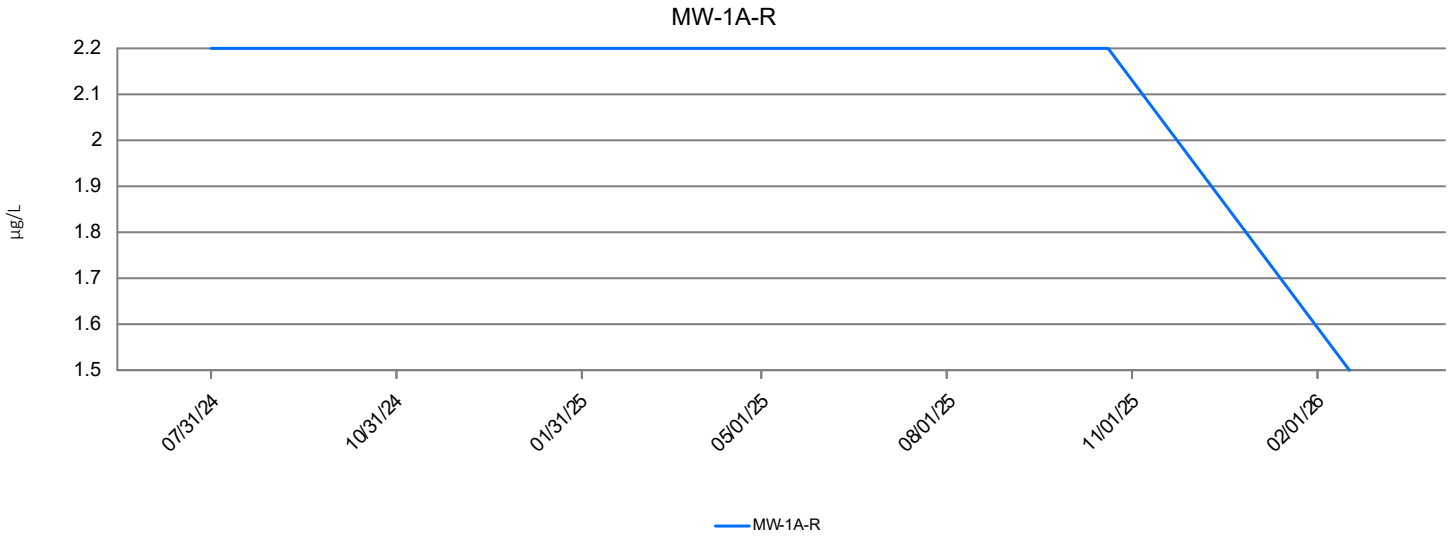
Variable Graphical Report

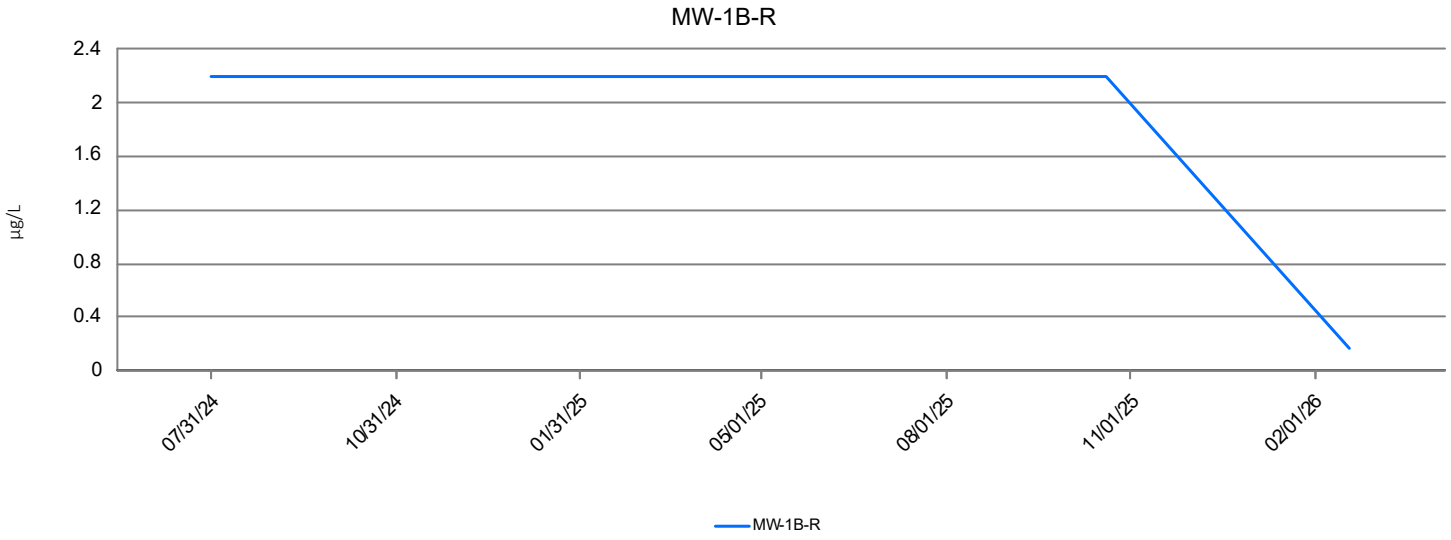
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Vanadium, Dissolved (µg/L)







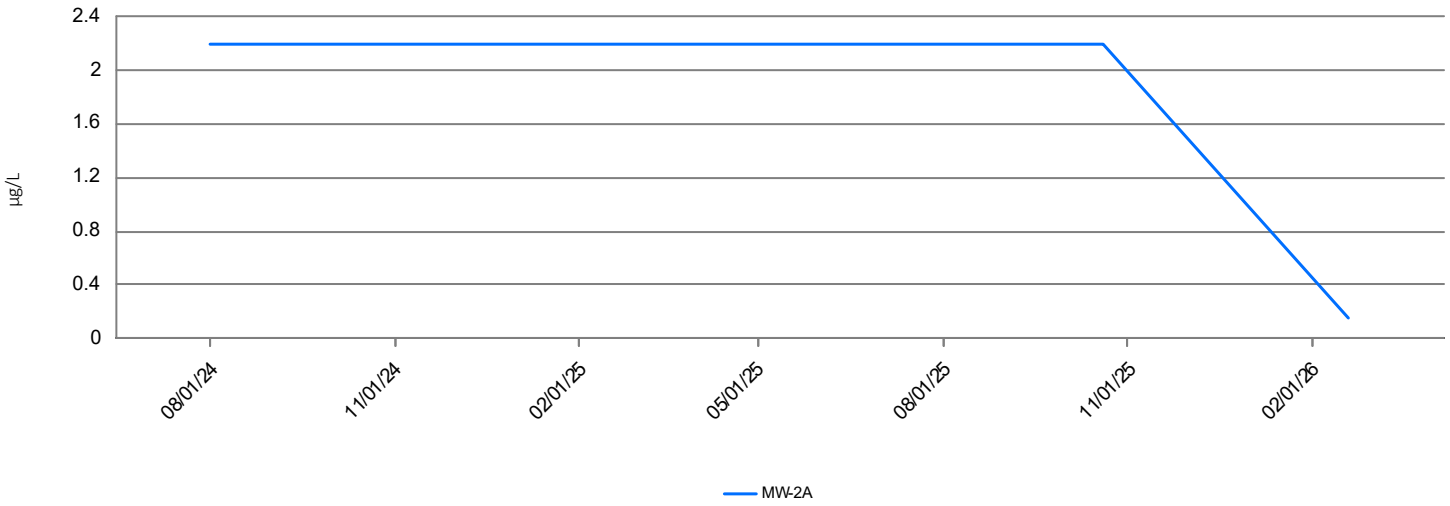
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

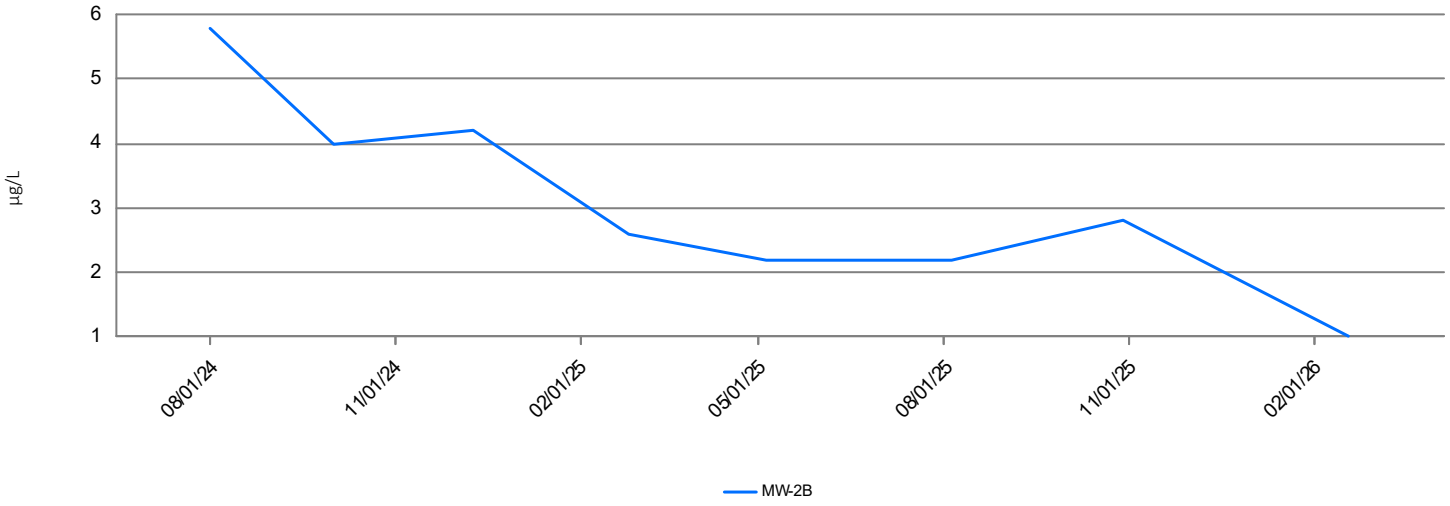
MonitorPro

No Group Selected, Vanadium, Dissolved (µg/L)

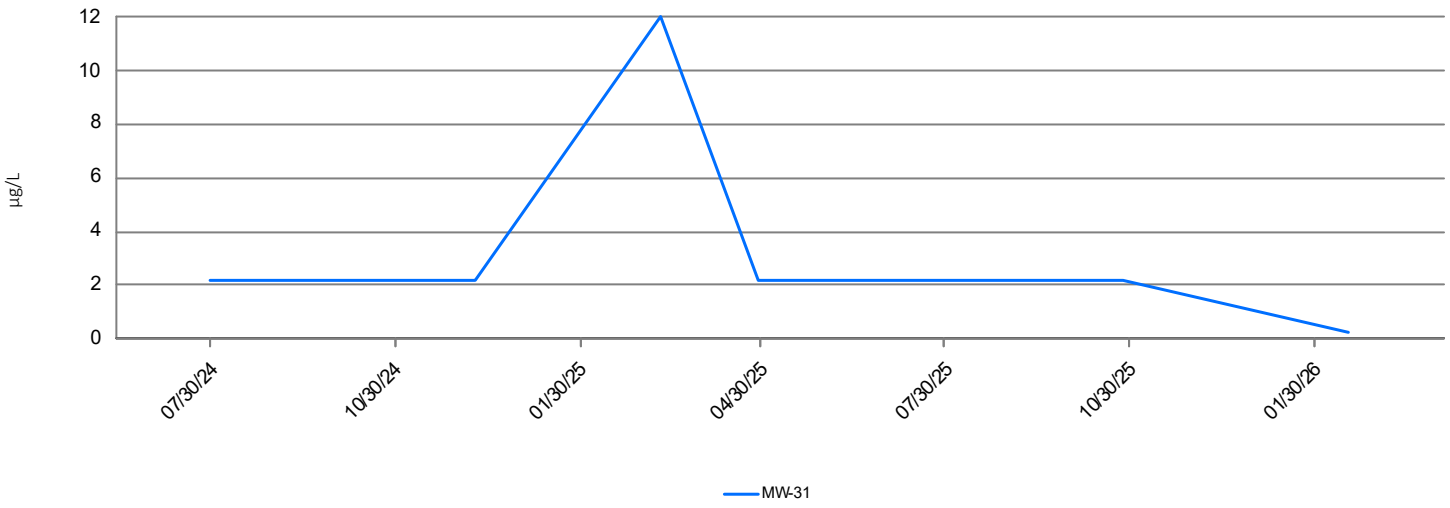
MW-2A



MW-2B



MW-31

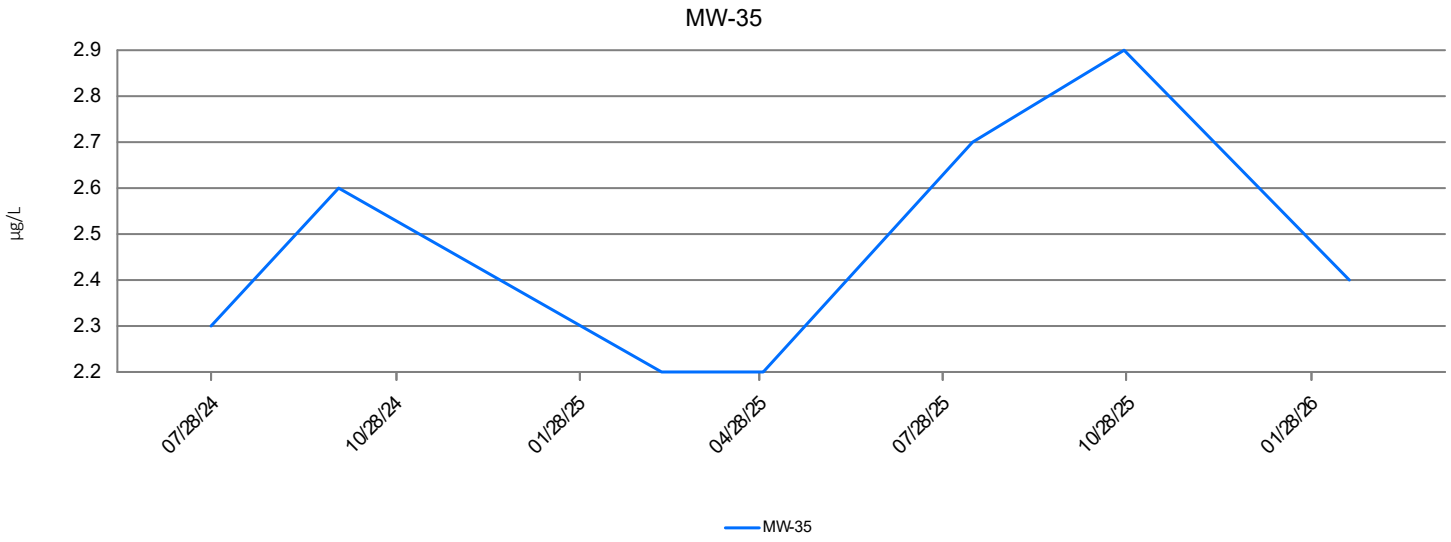


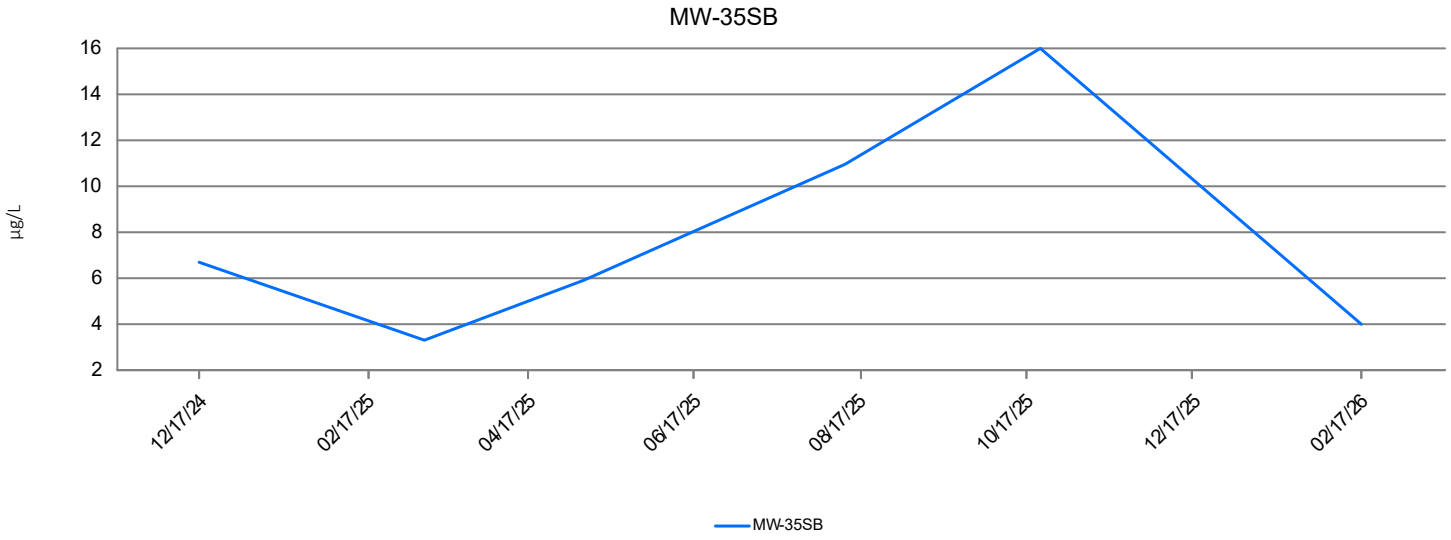
Variable Graphical Report

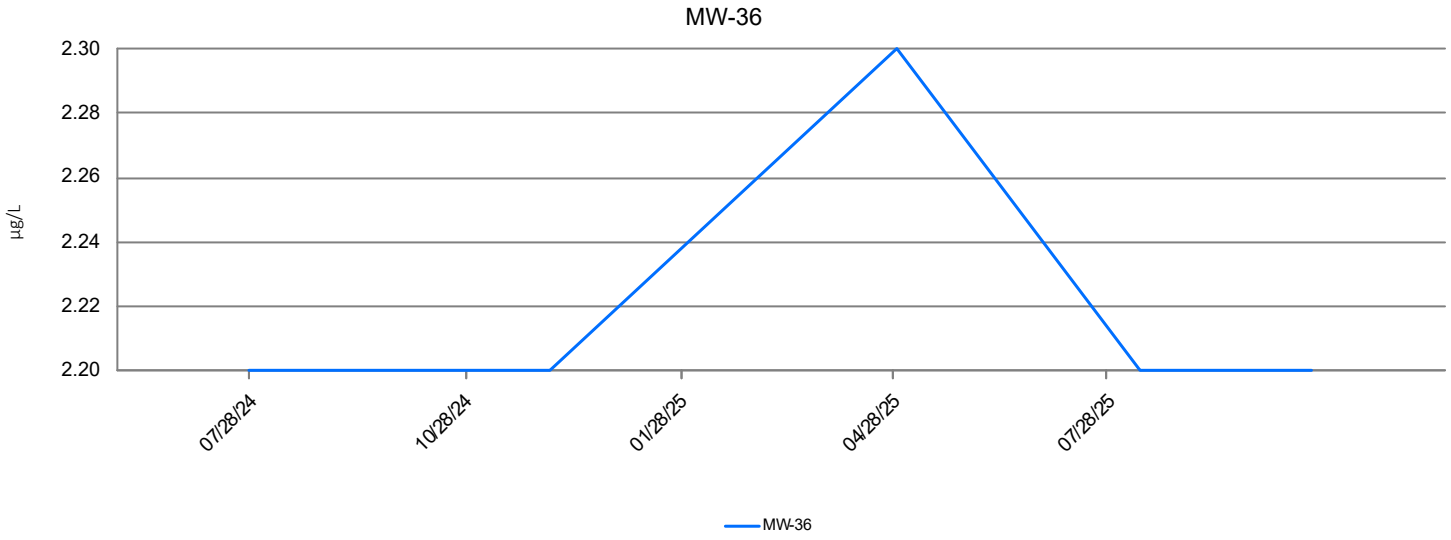
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Vanadium, Dissolved (µg/L)





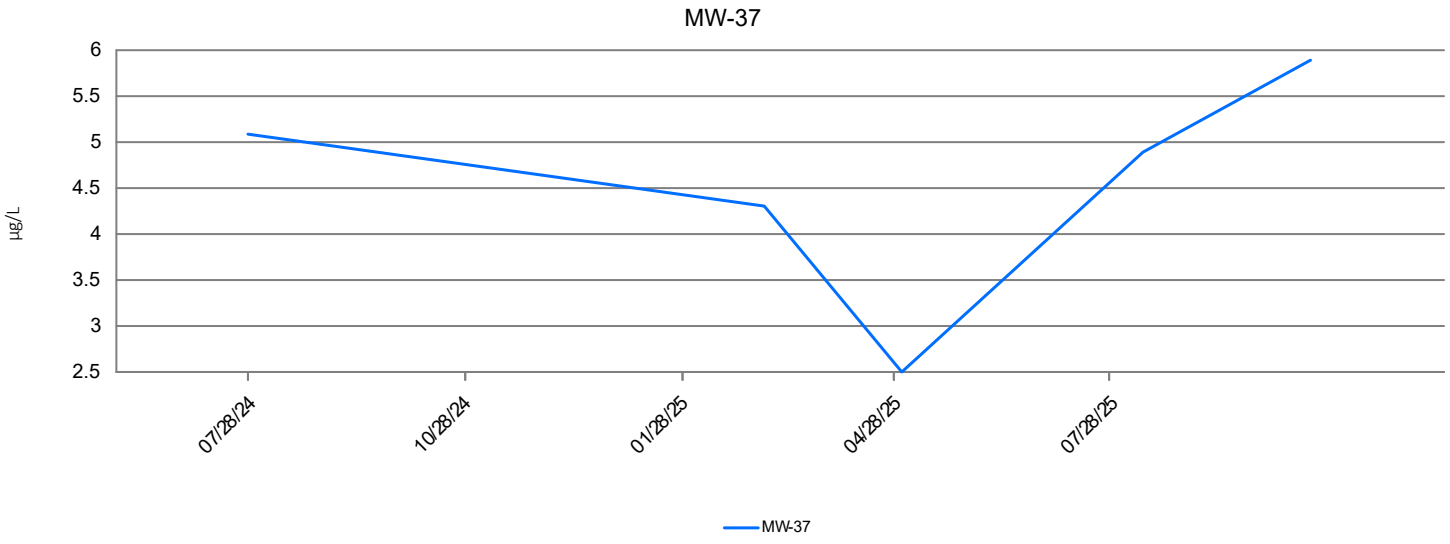


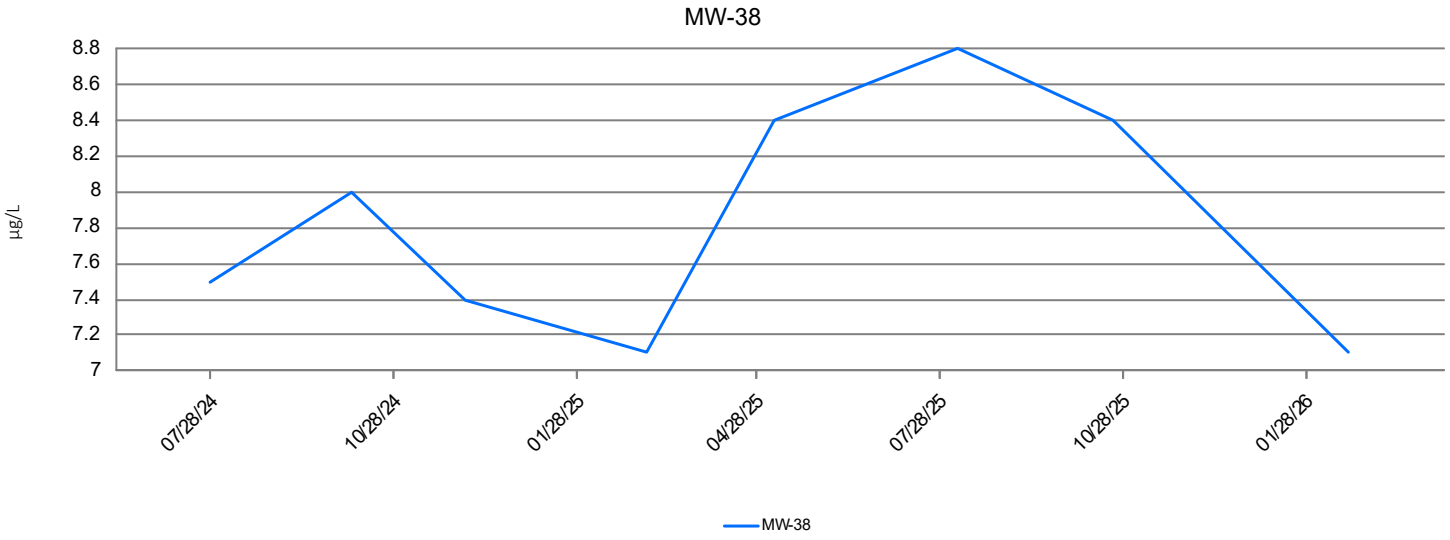
Variable Graphical Report

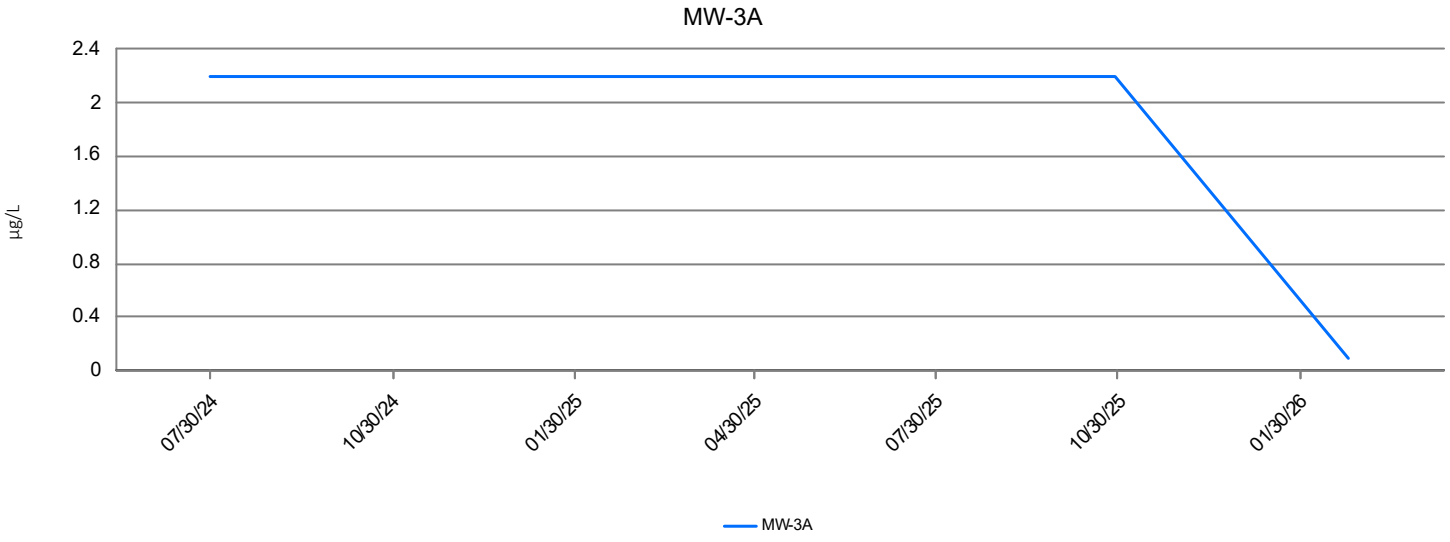
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Vanadium, Dissolved (µg/L)





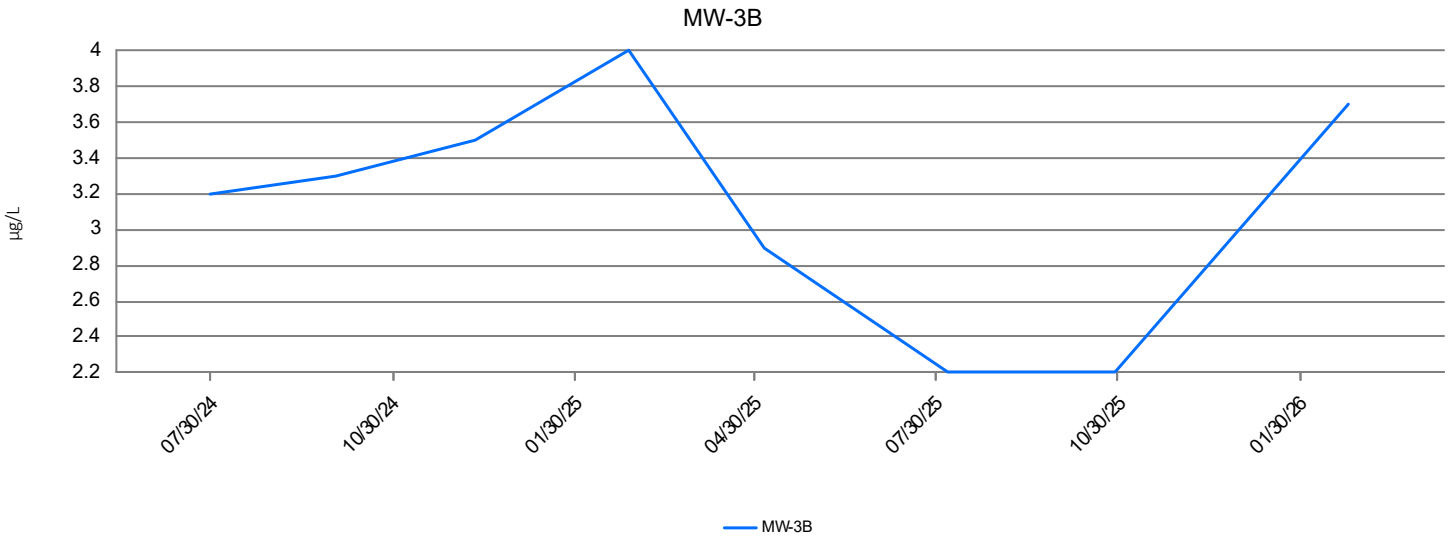


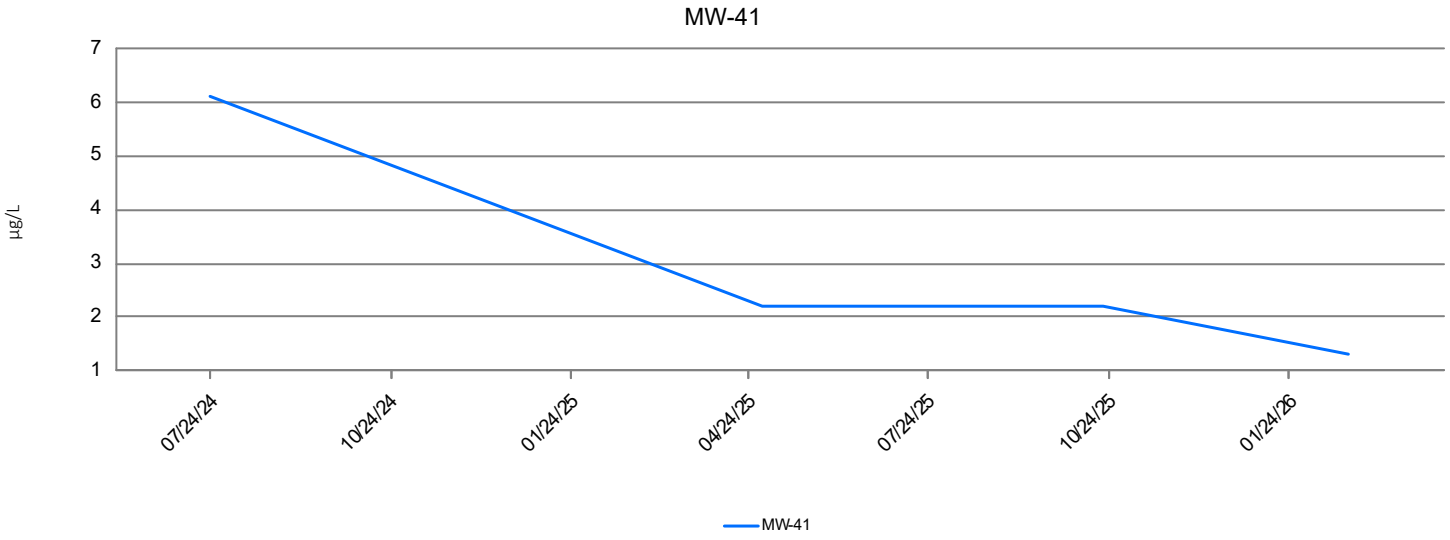
Variable Graphical Report

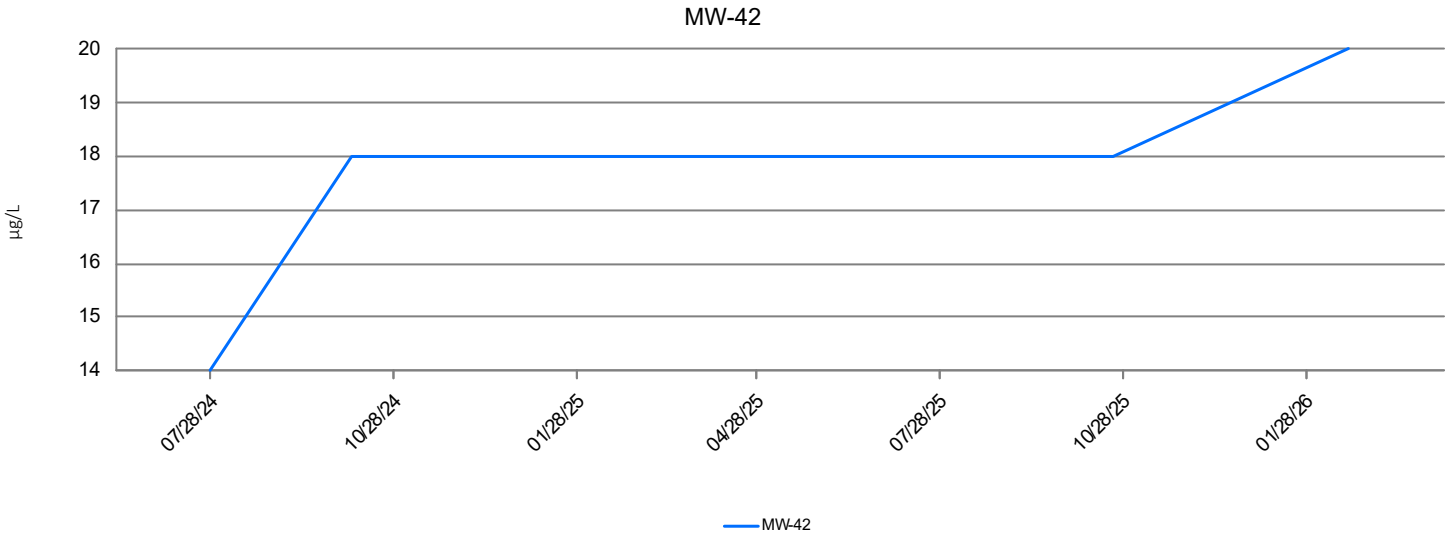
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Vanadium, Dissolved (µg/L)







Printed Date: 05/21/2026

EHS DATA

MCERTS Cert. no. Sira MC090140/02

MCERTS

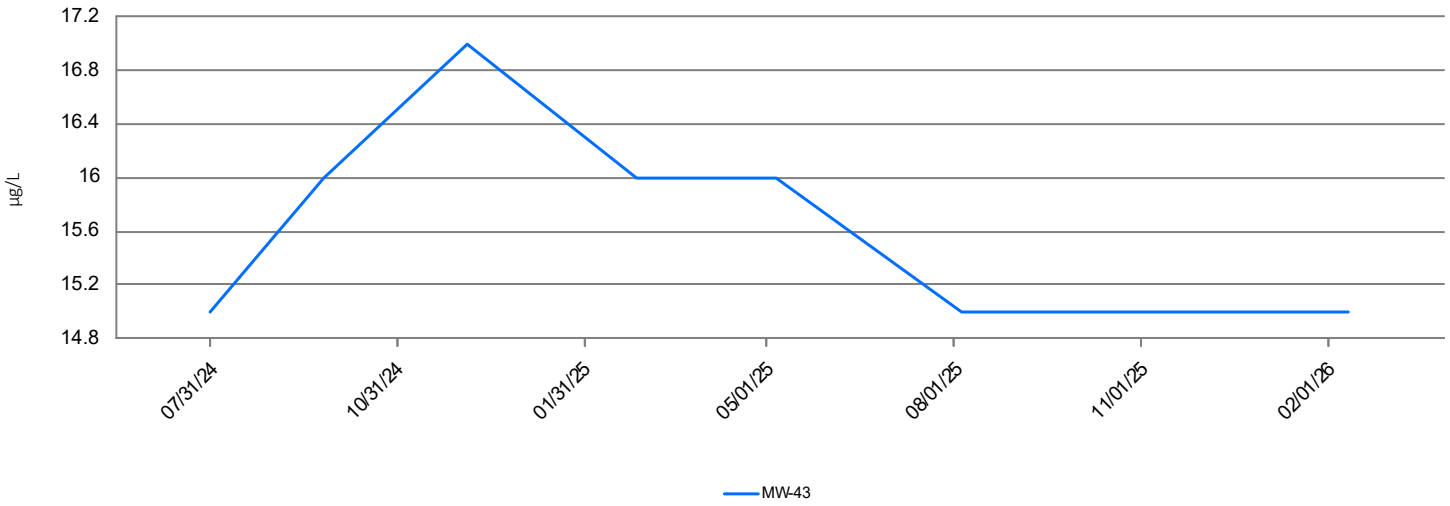
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

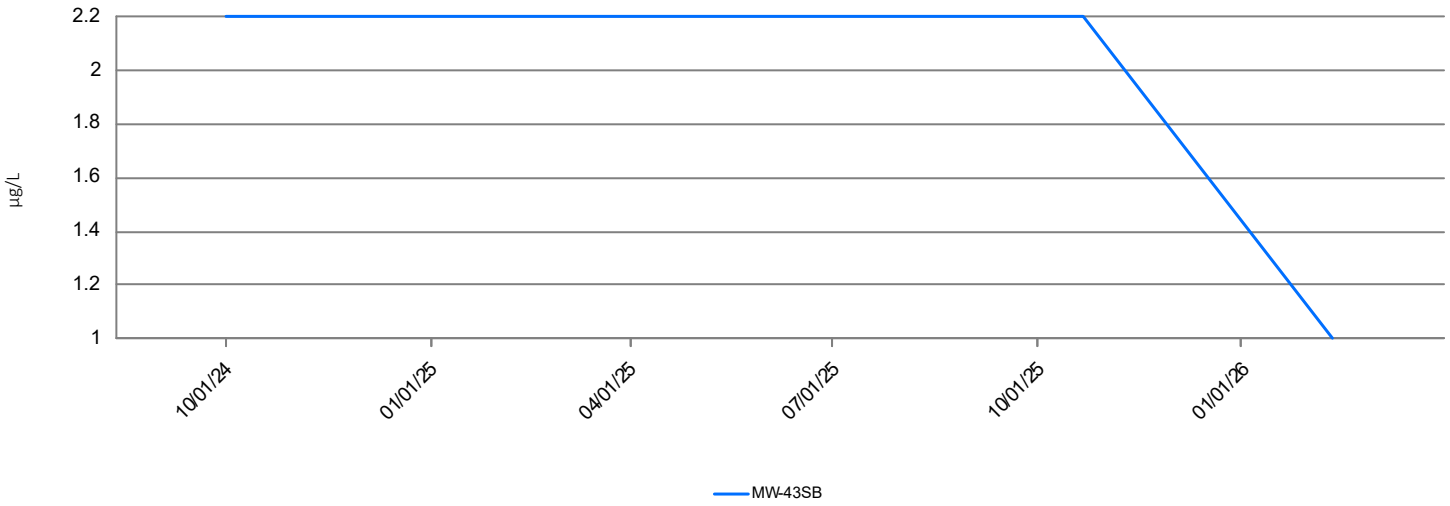
MonitorPro

No Group Selected, Vanadium, Dissolved (µg/L)

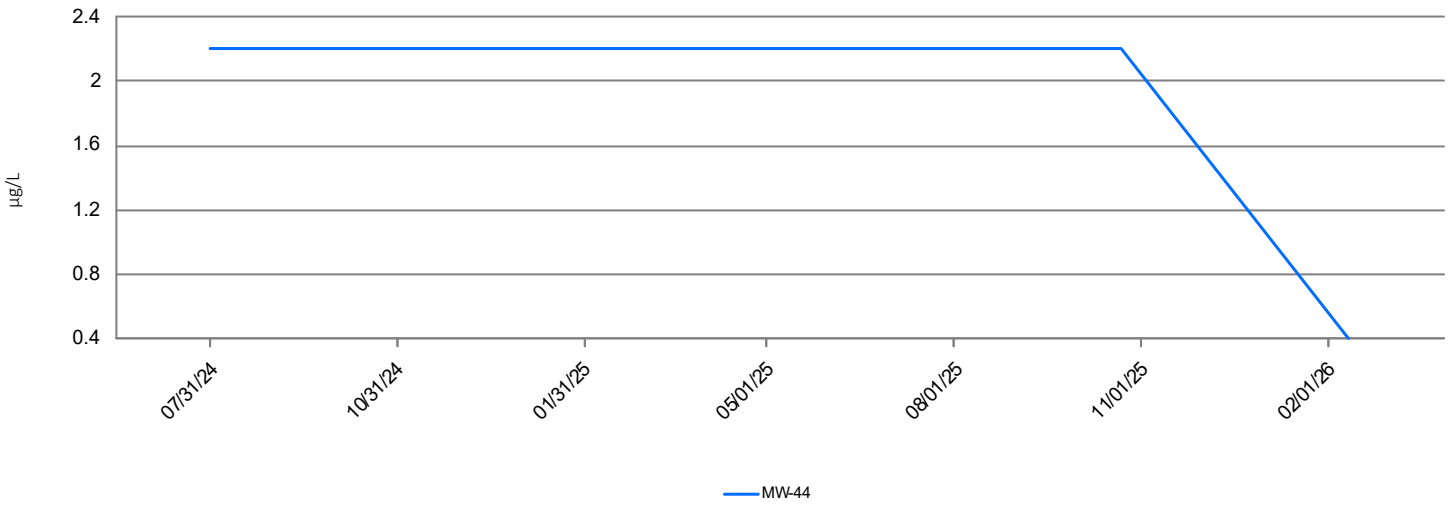
MW-43



MW-43SB



MW-44



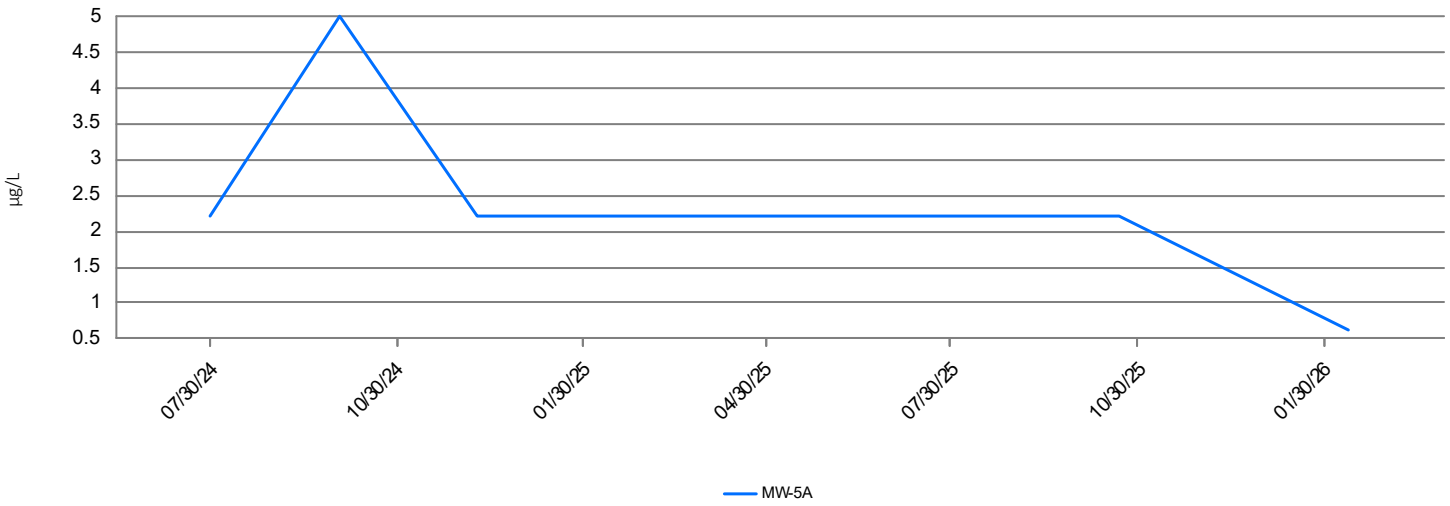
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

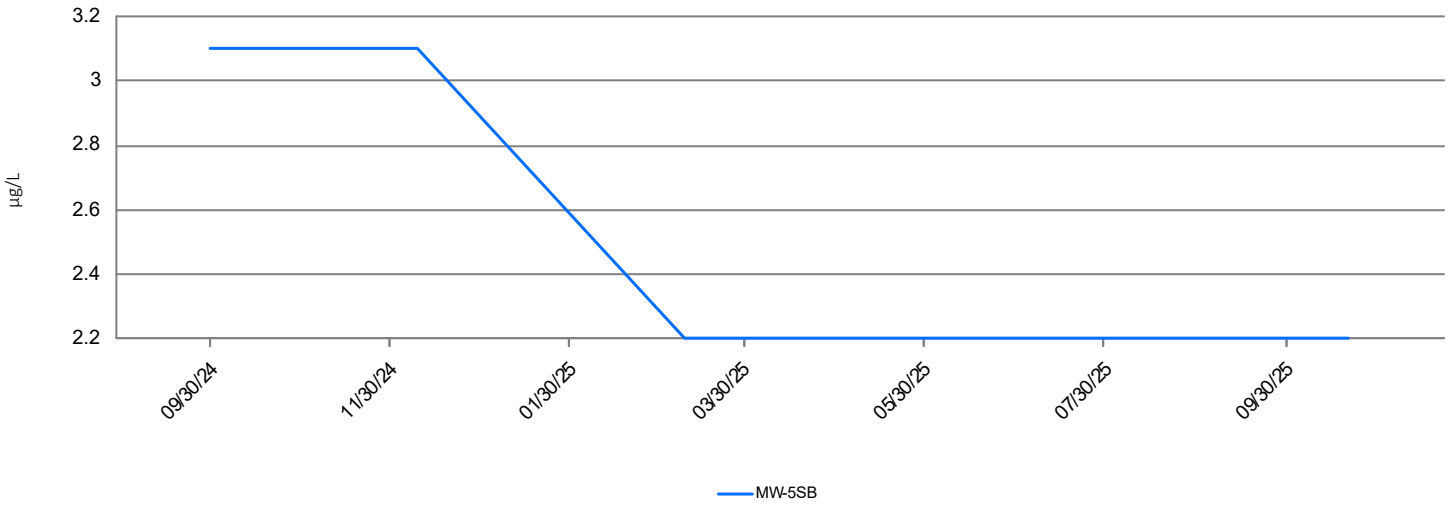
MonitorPro

No Group Selected, Vanadium, Dissolved (µg/L)

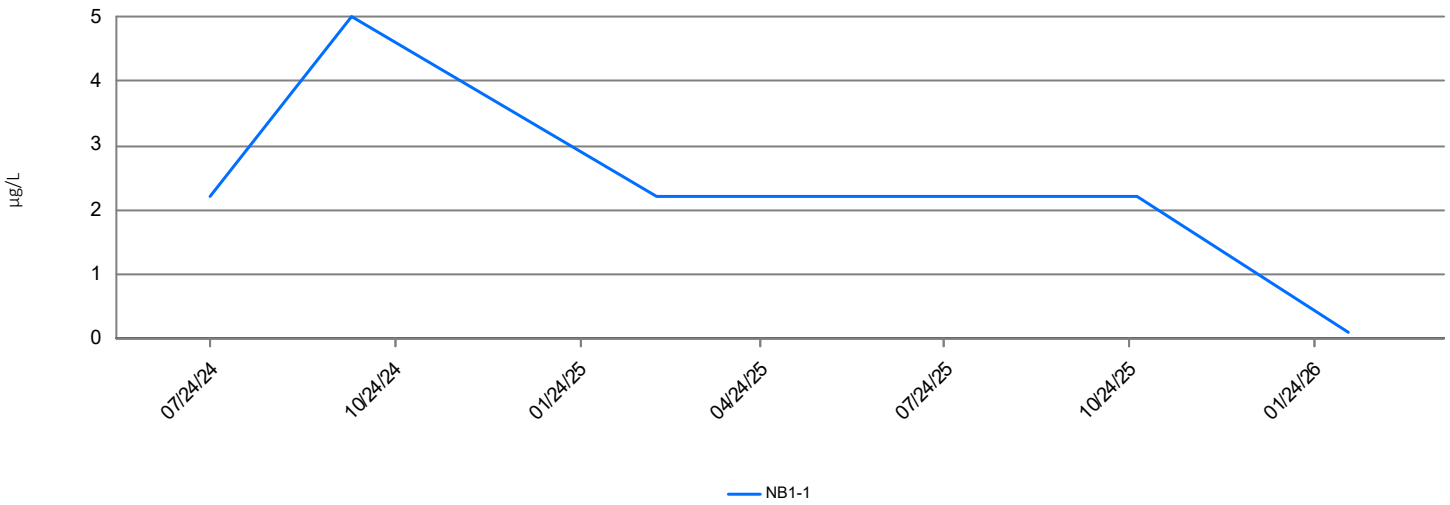
MW-5A



MW-5SB



NB1-1

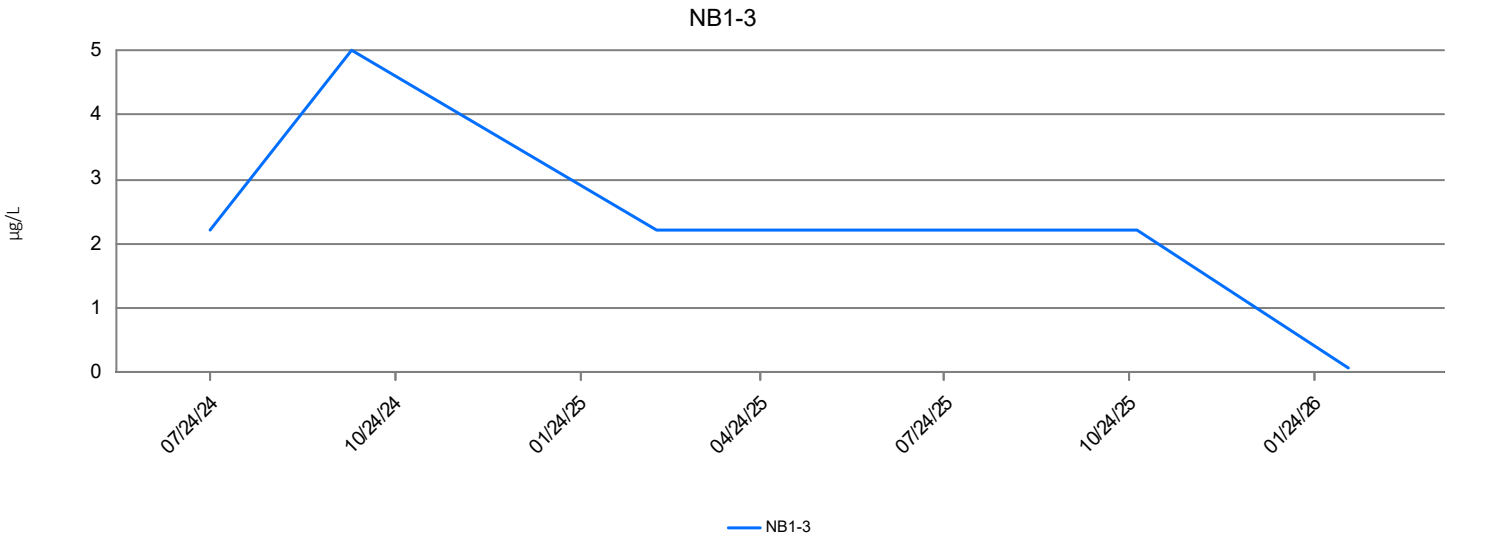


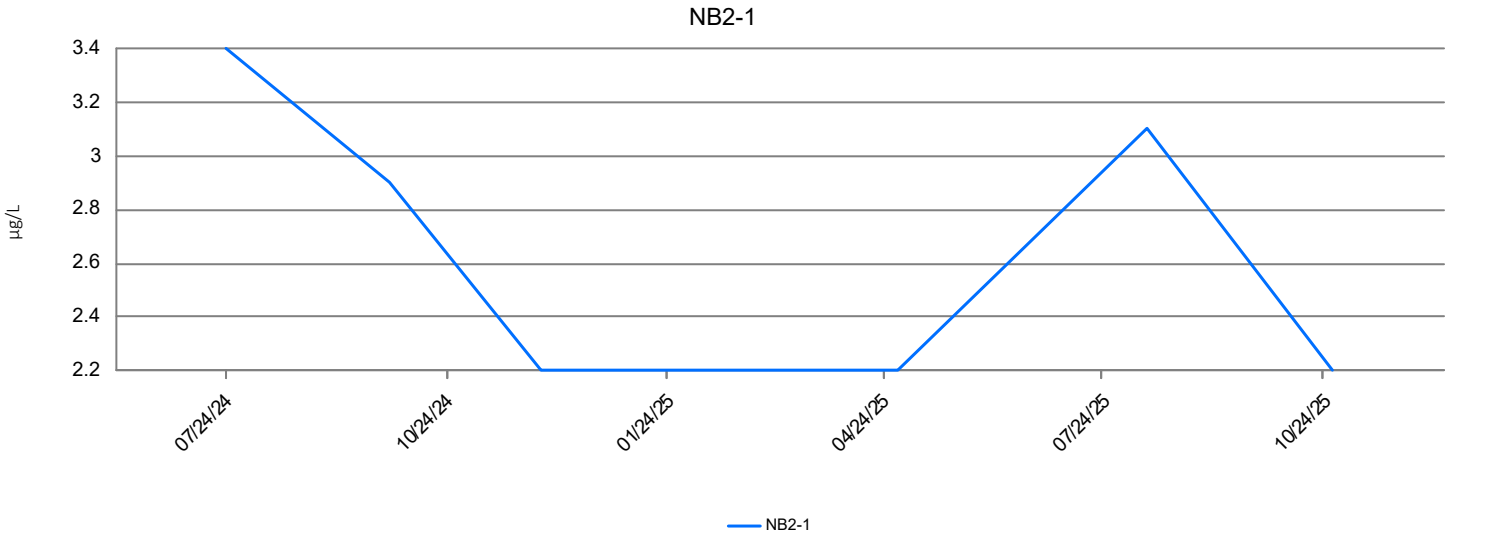
Variable Graphical Report

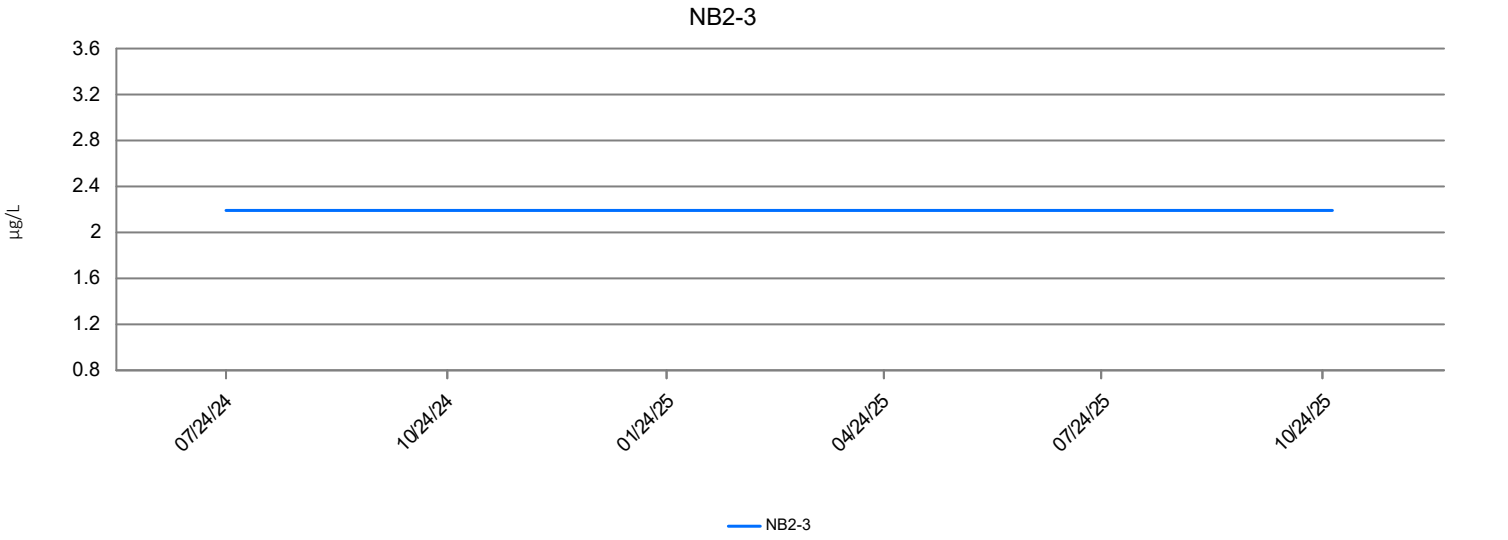
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Vanadium, Dissolved (µg/L)







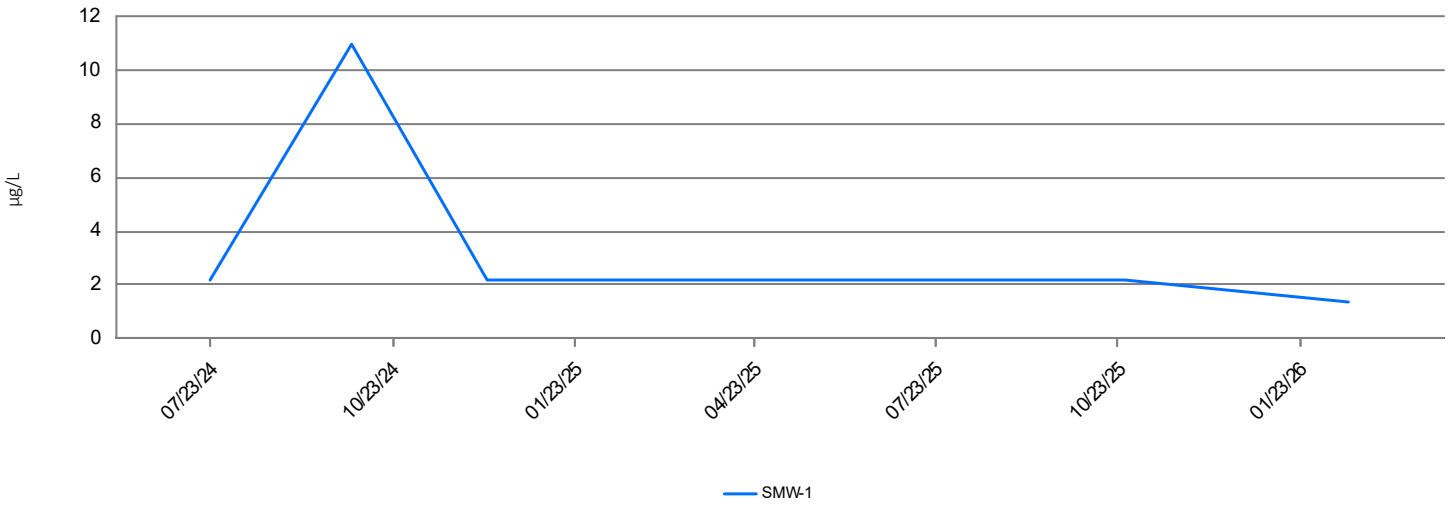
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

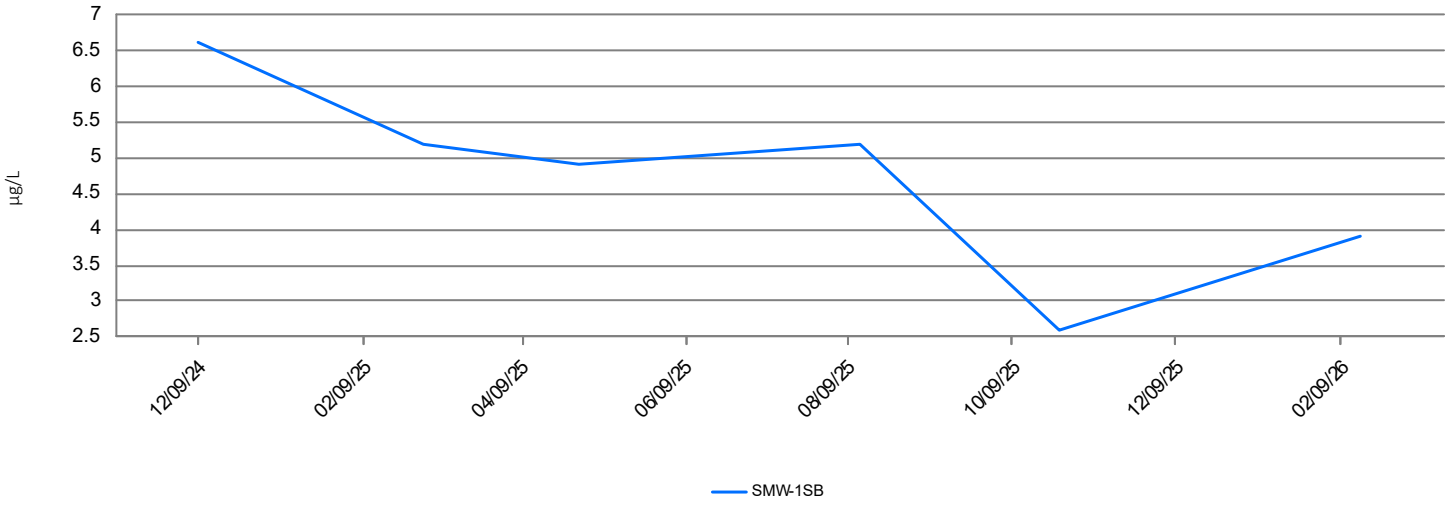
MonitorPro

No Group Selected, Vanadium, Dissolved (µg/L)

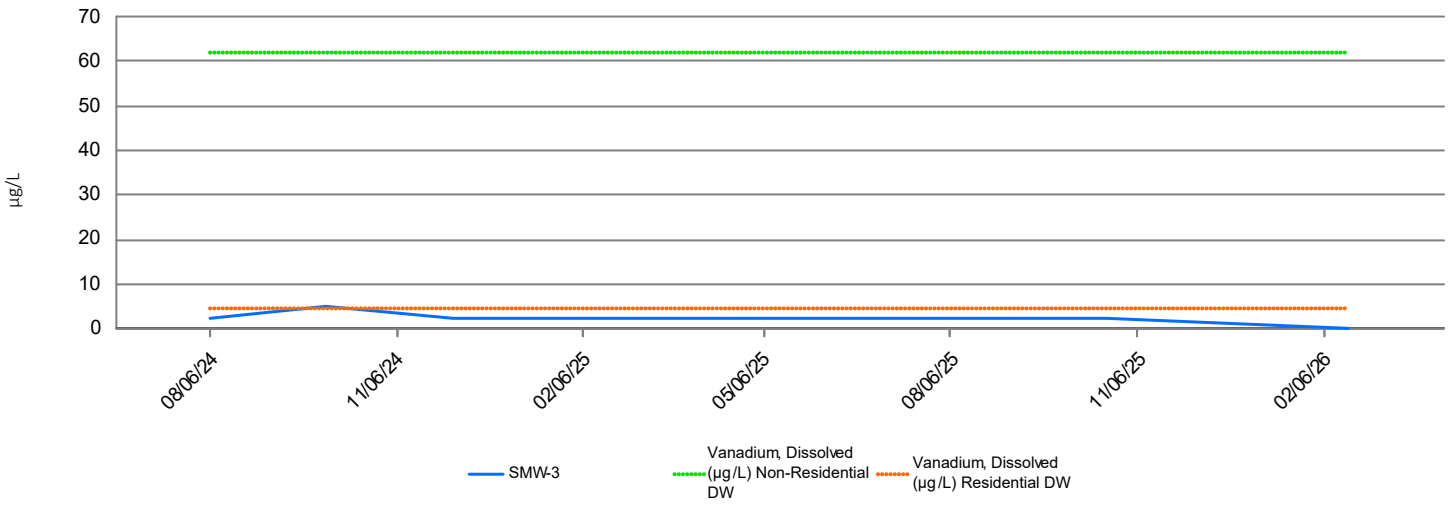
SMW-1



SMW-1SB



SMW-3



Printed Date: 05/21/2026

EHS DATA

MCERTS Cert. no. Sira MC090140/02

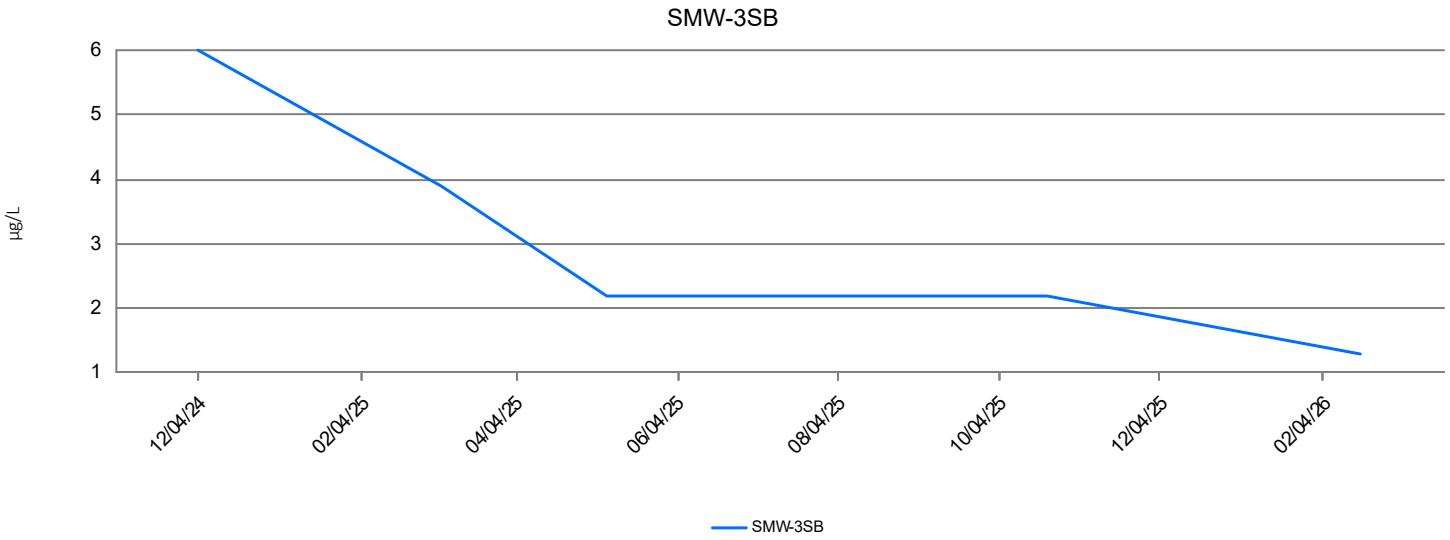
MCERTS

Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Vanadium, Dissolved (µg/L)



Printed Date: 05/21/2026

EHS DATA

MCERTS Cert. no. Sira MC090140/02

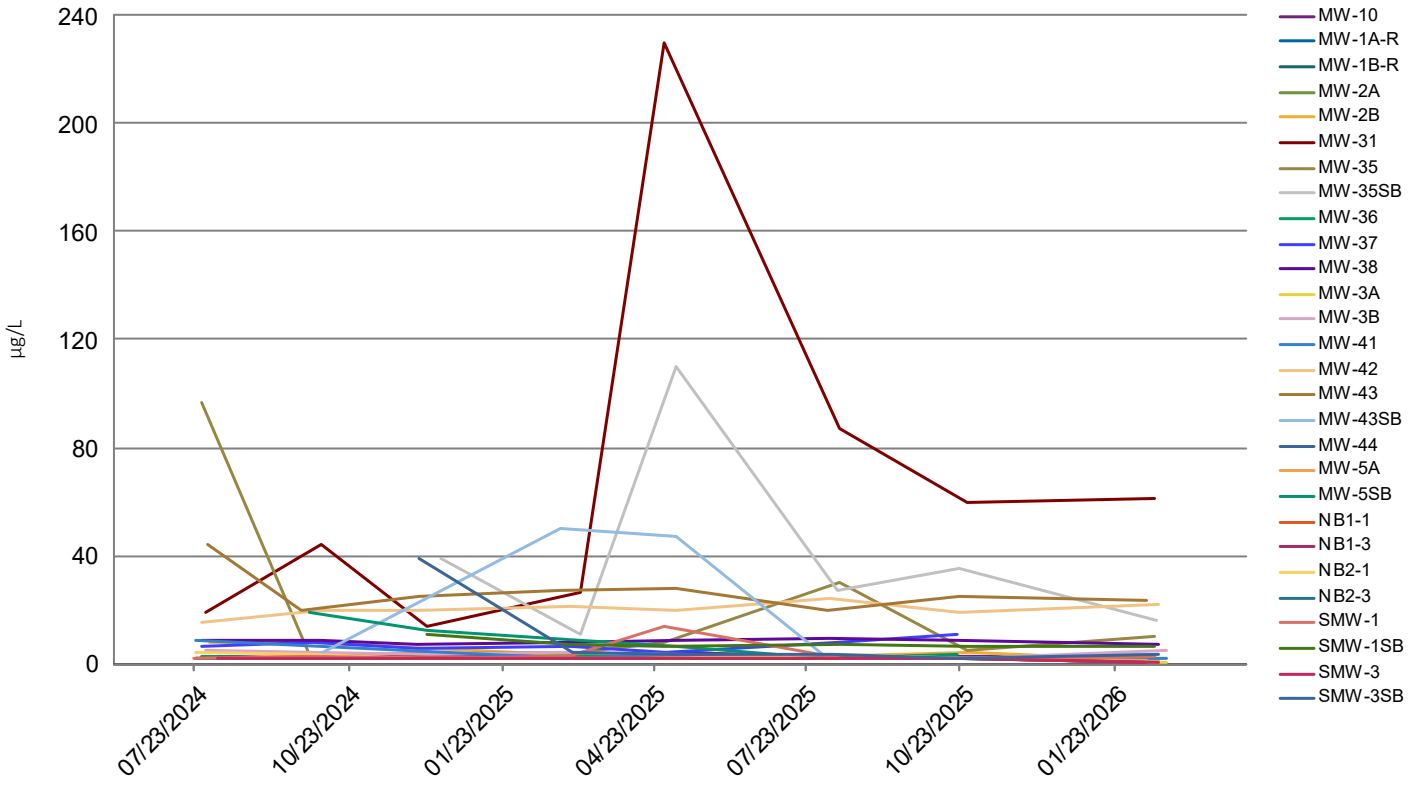
MCERTS

Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Vanadium, Total Recoverable (µg/L)

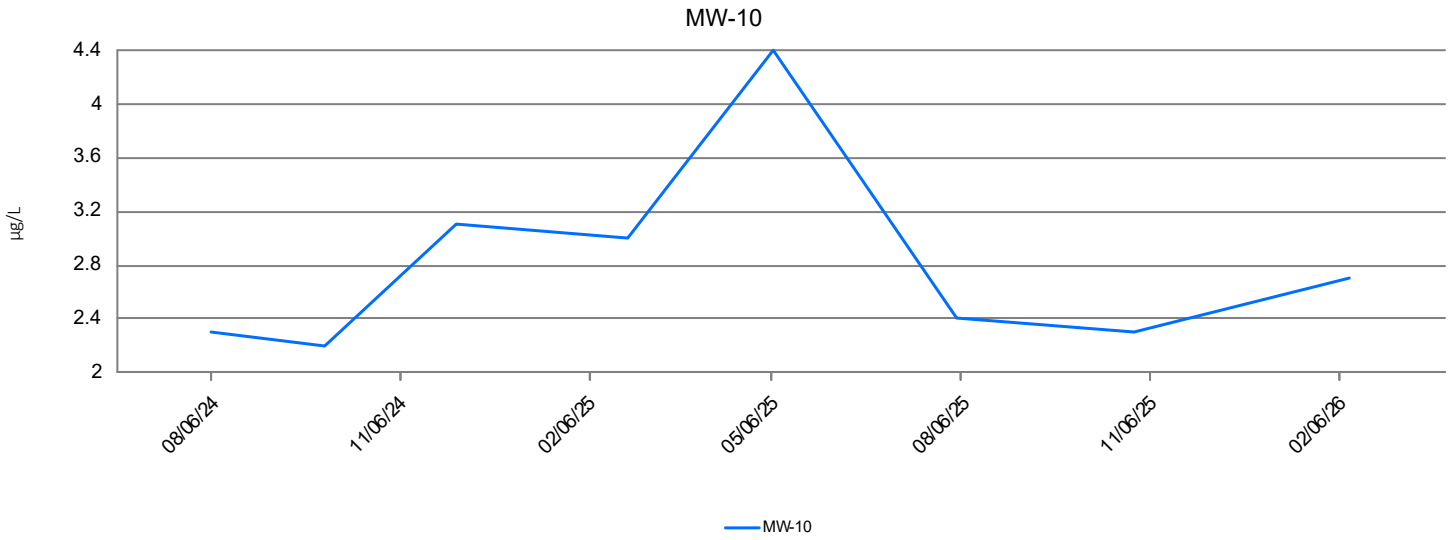


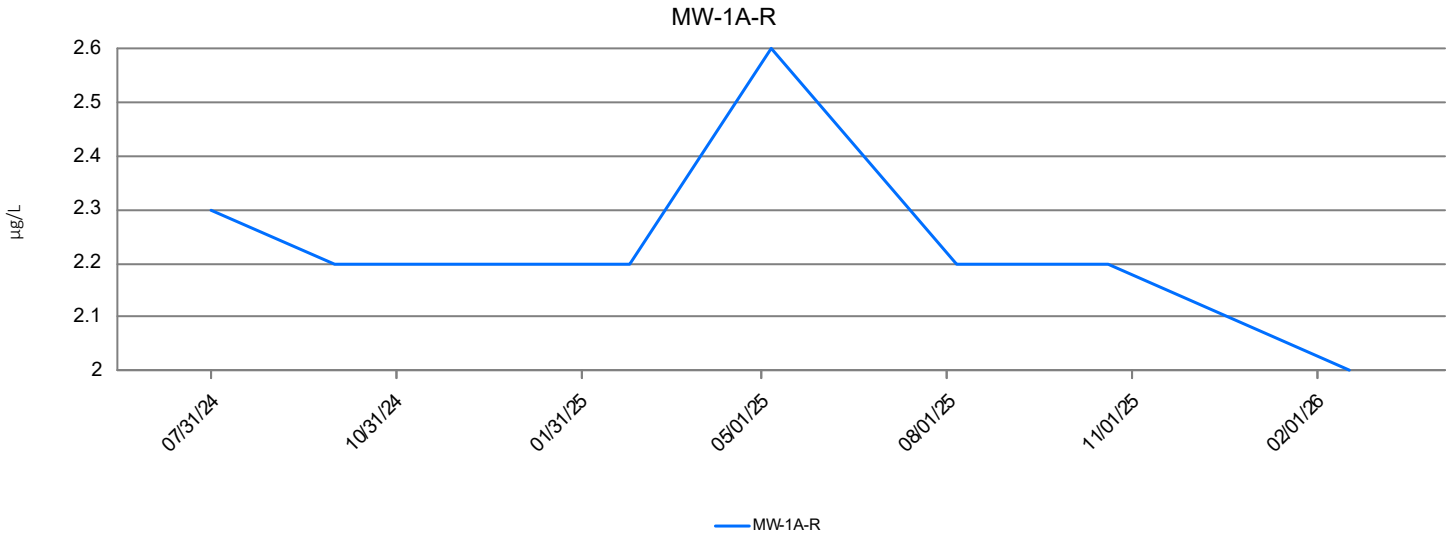
Variable Graphical Report

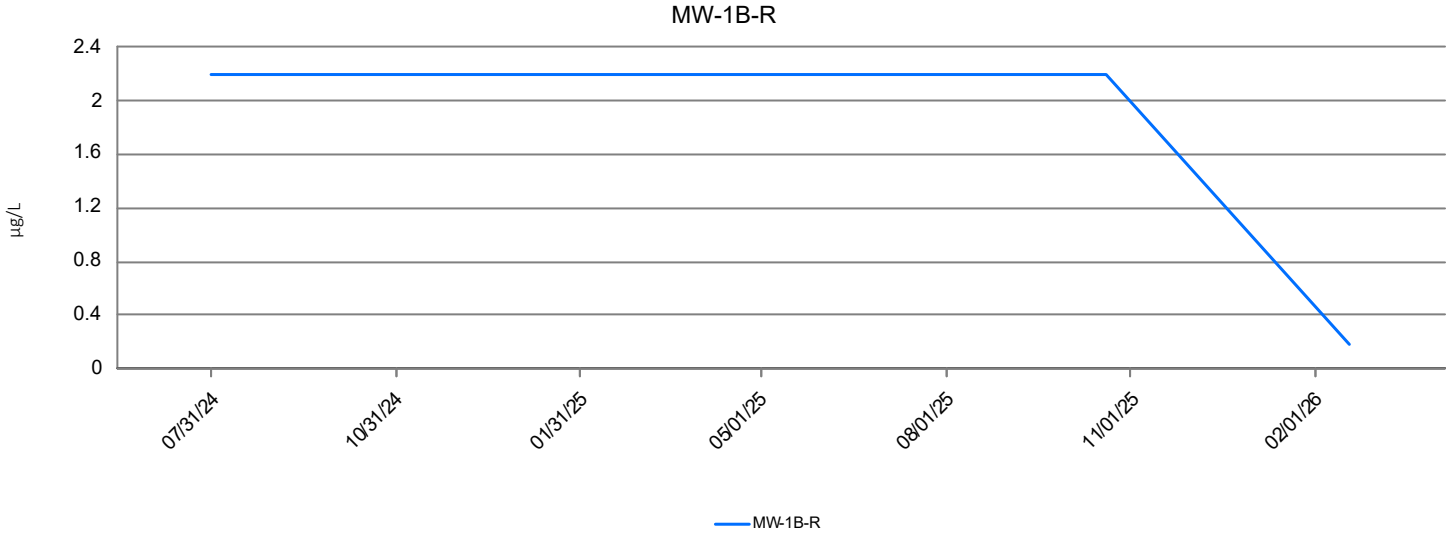
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Vanadium, Total Recoverable (µg/L)





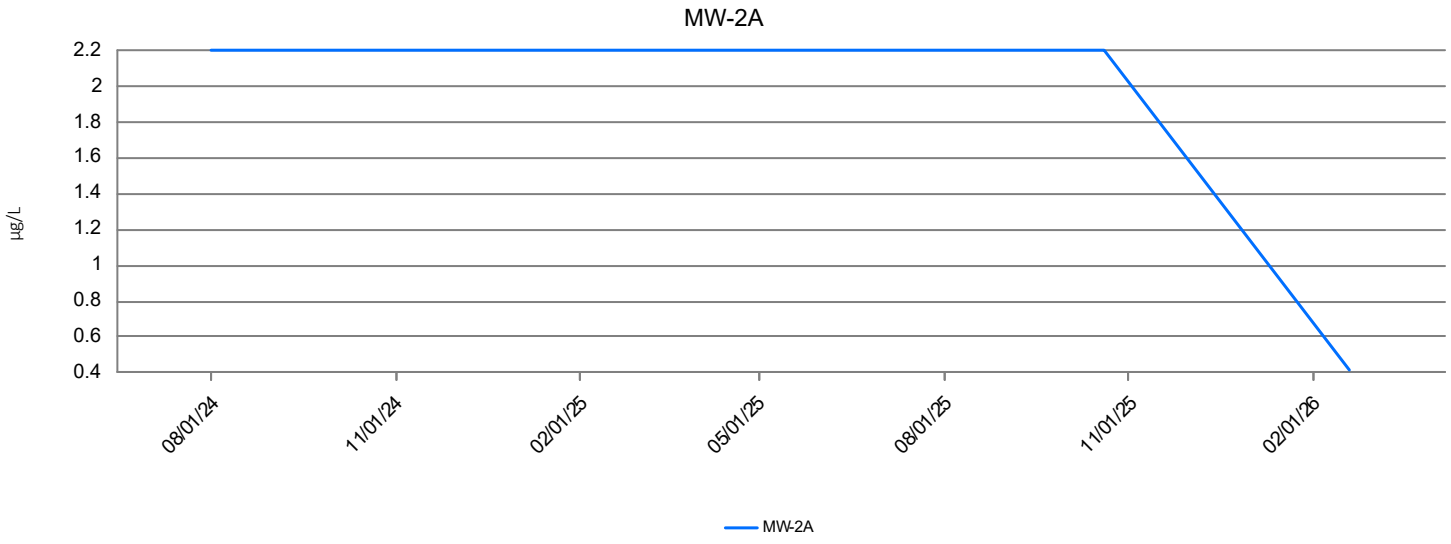


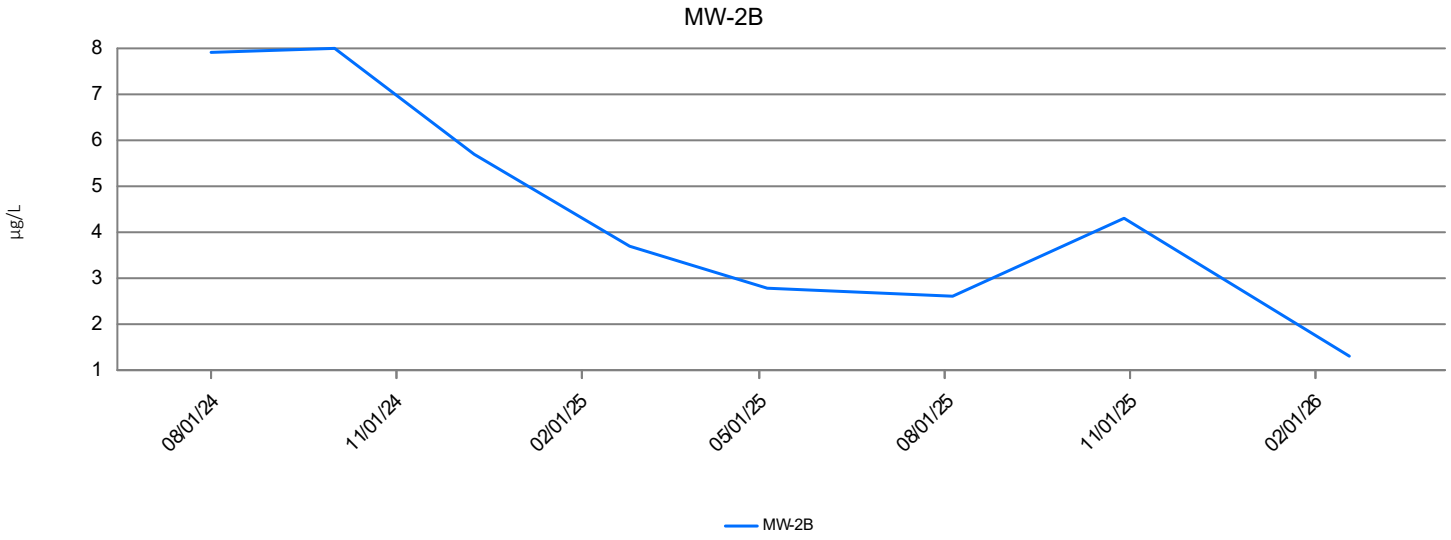
Variable Graphical Report

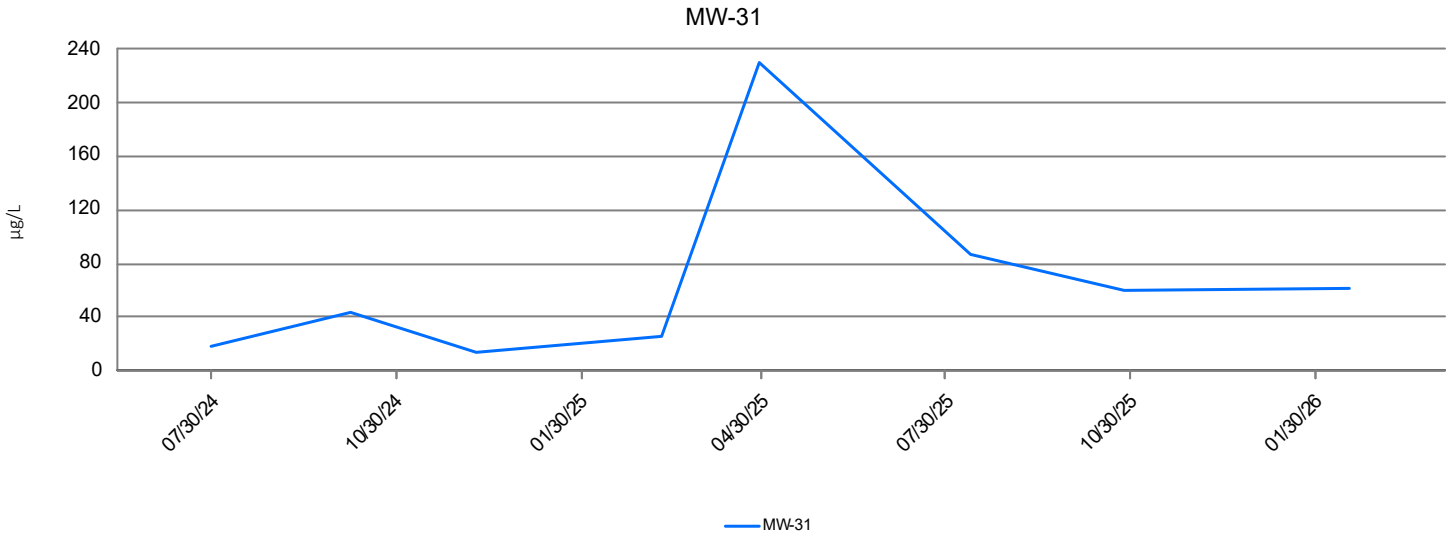
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Vanadium, Total Recoverable (µg/L)







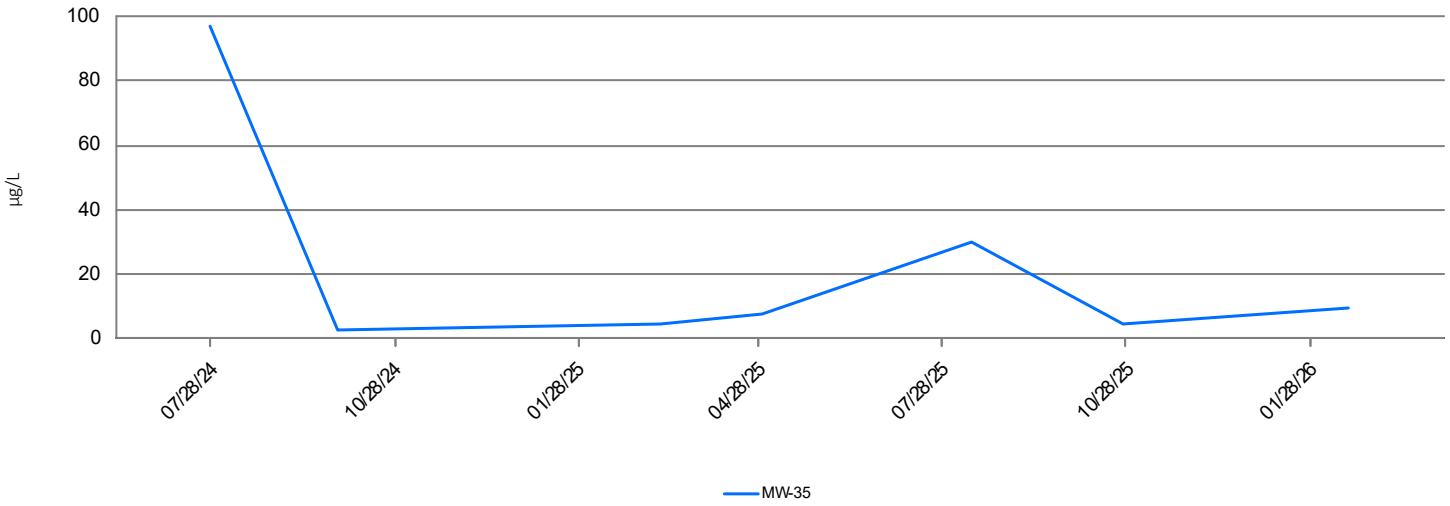
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

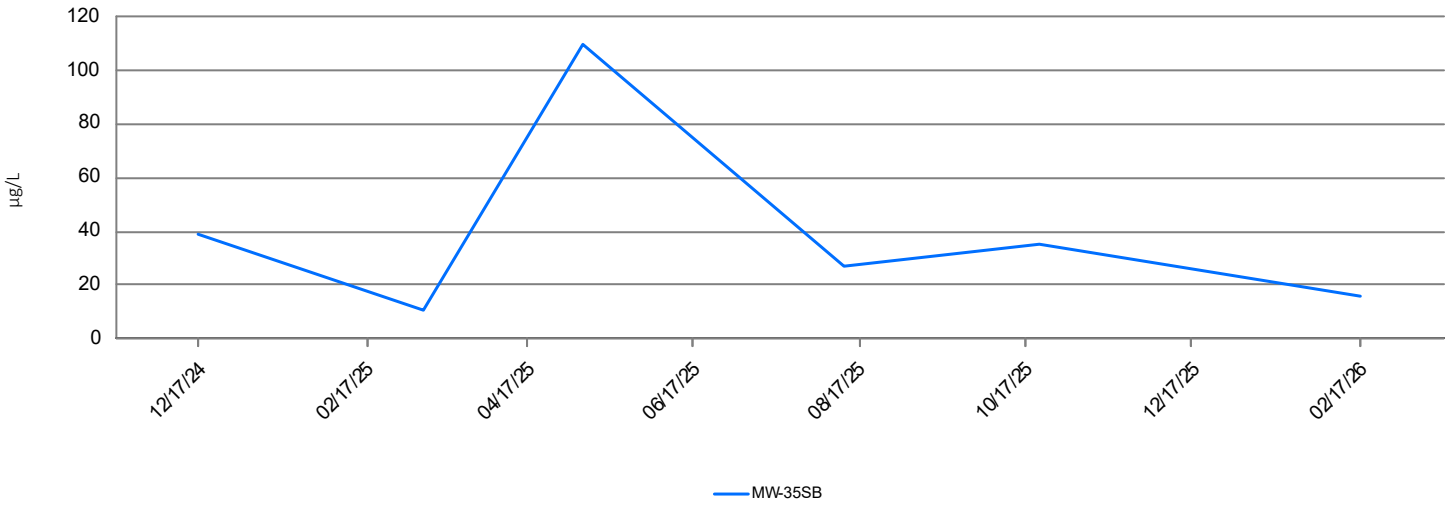
MonitorPro

No Group Selected, Vanadium, Total Recoverable (µg/L)

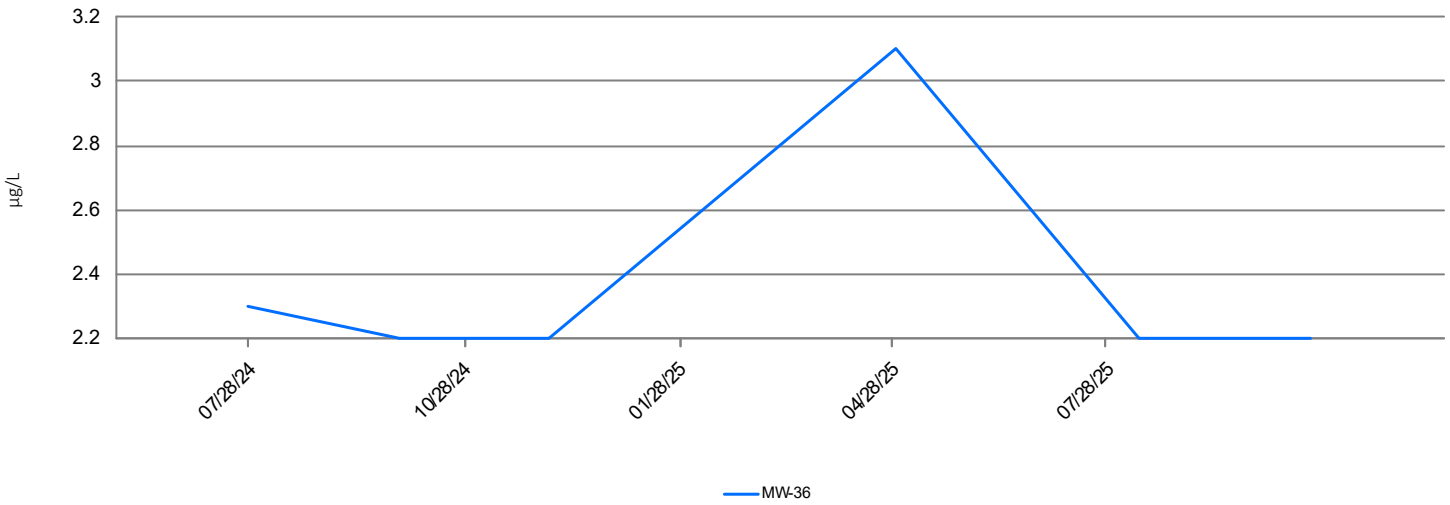
MW-35



MW-35SB



MW-36

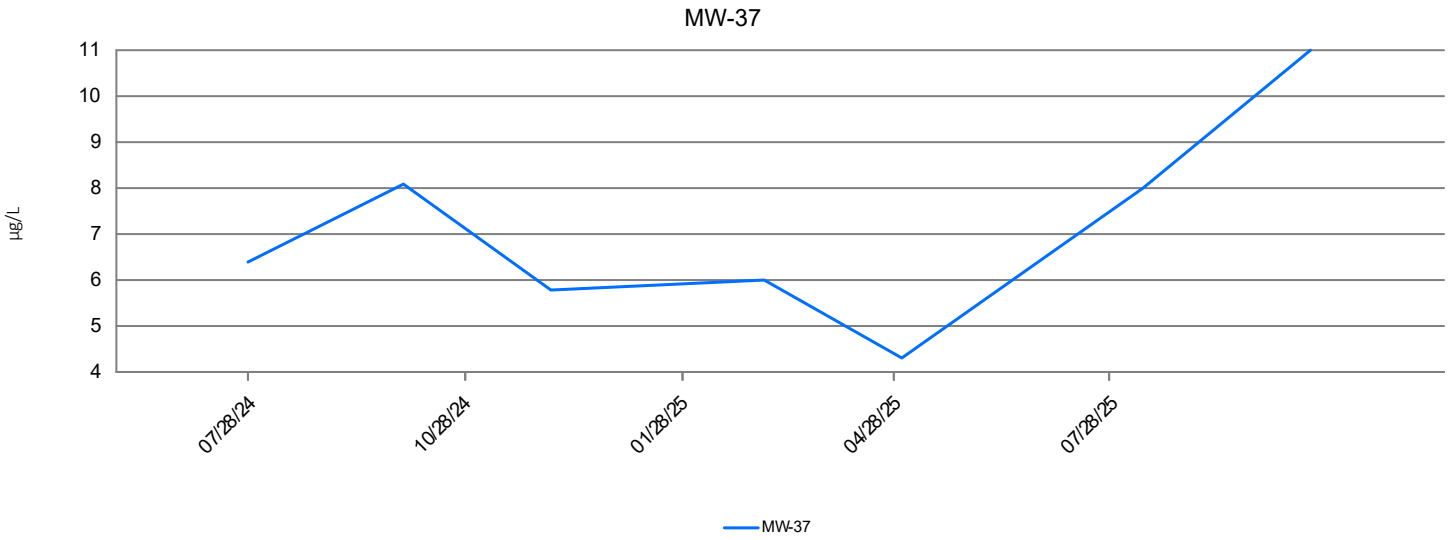


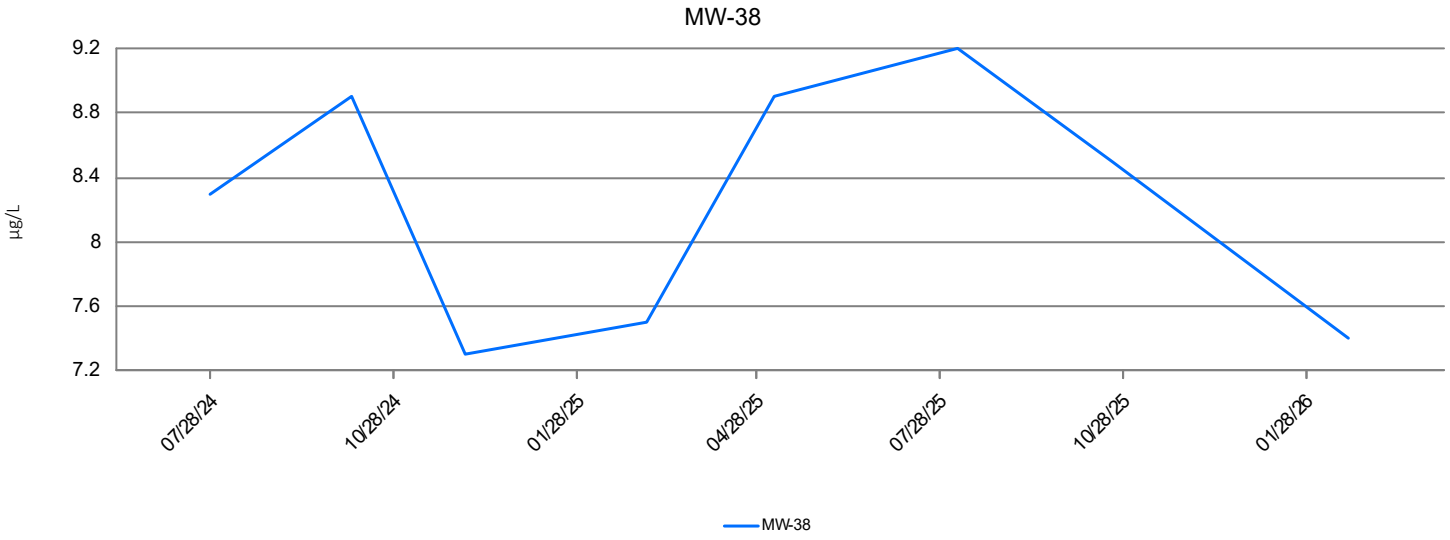
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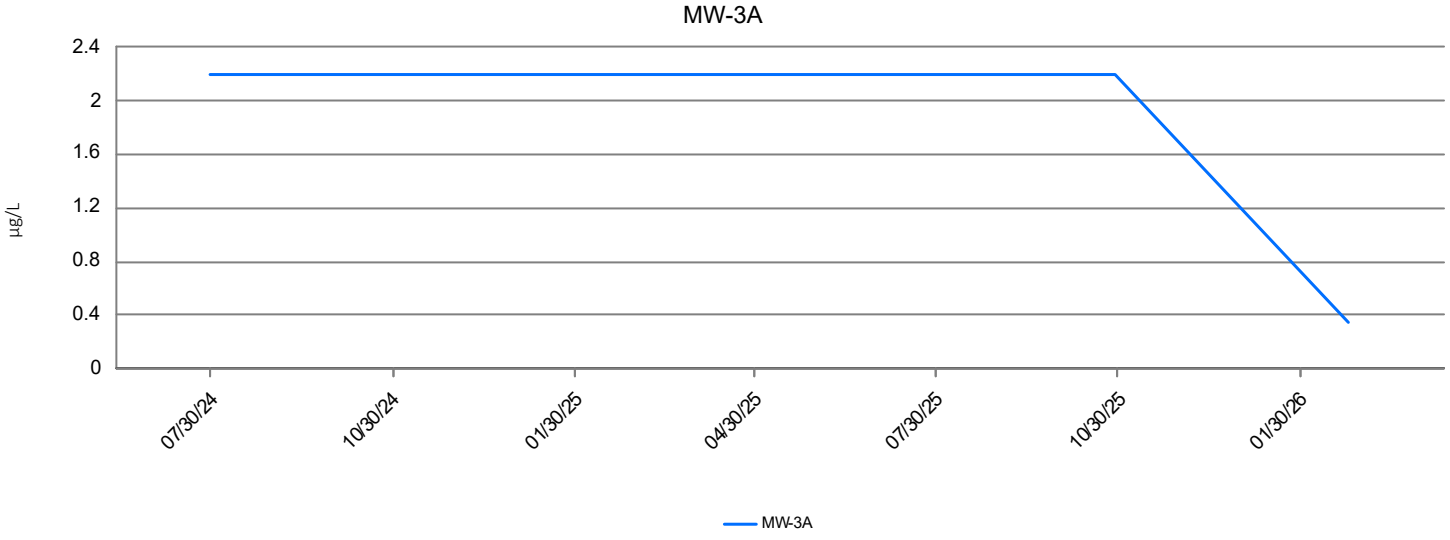
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Vanadium, Total Recoverable (µg/L)







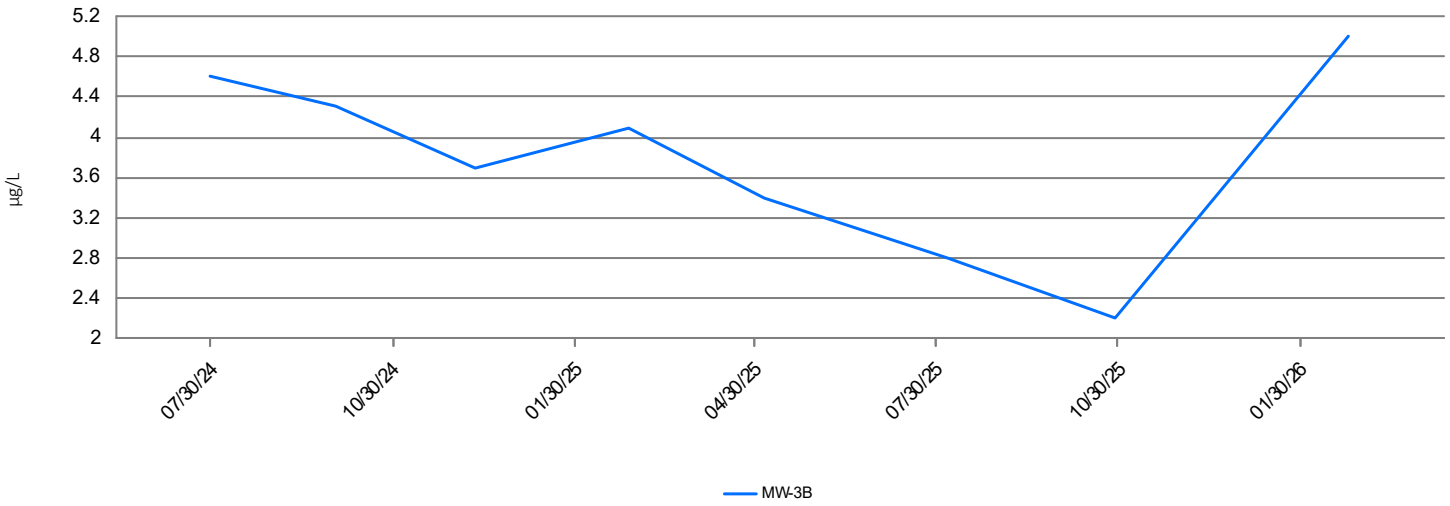
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

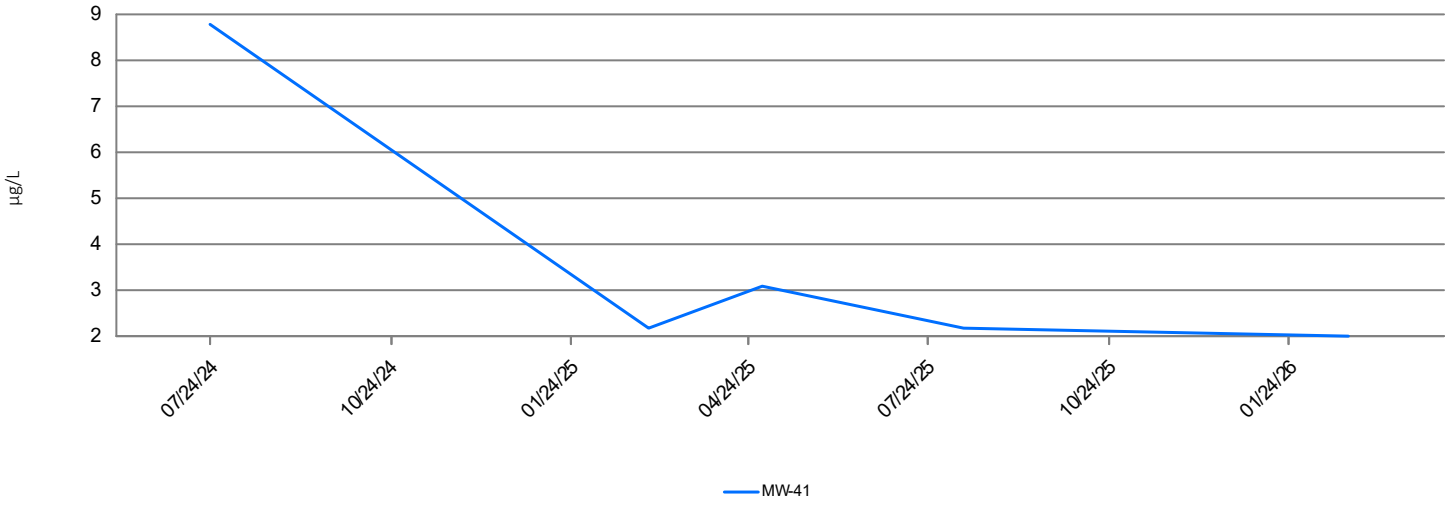
MonitorPro

No Group Selected, Vanadium, Total Recoverable (µg/L)

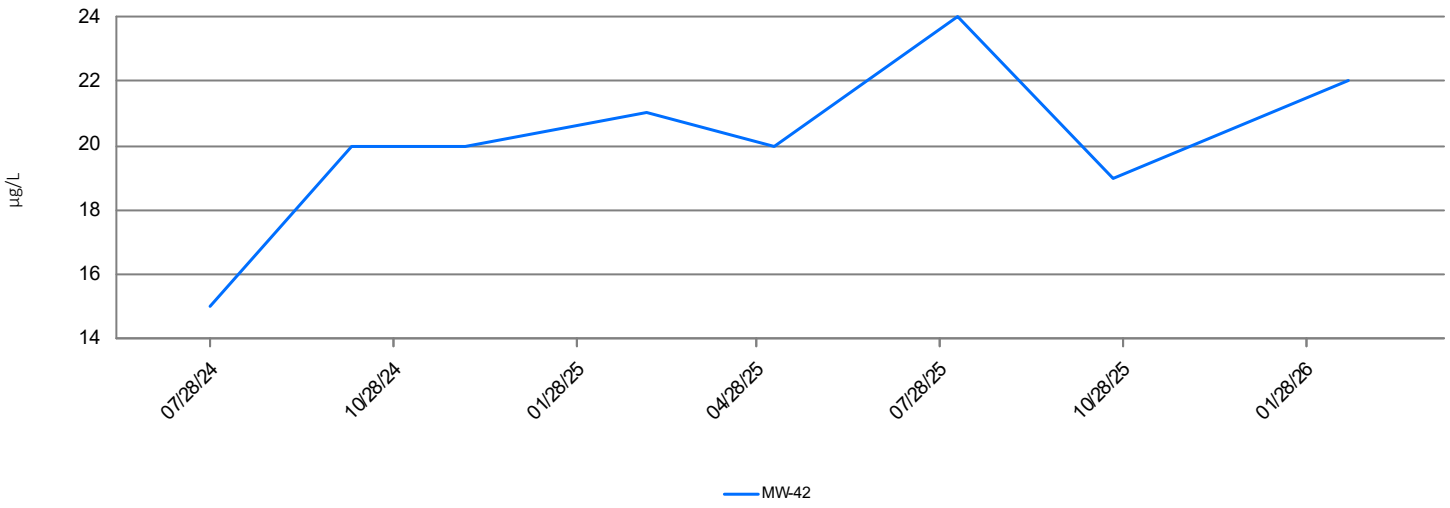
MW-3B



MW-41



MW-42

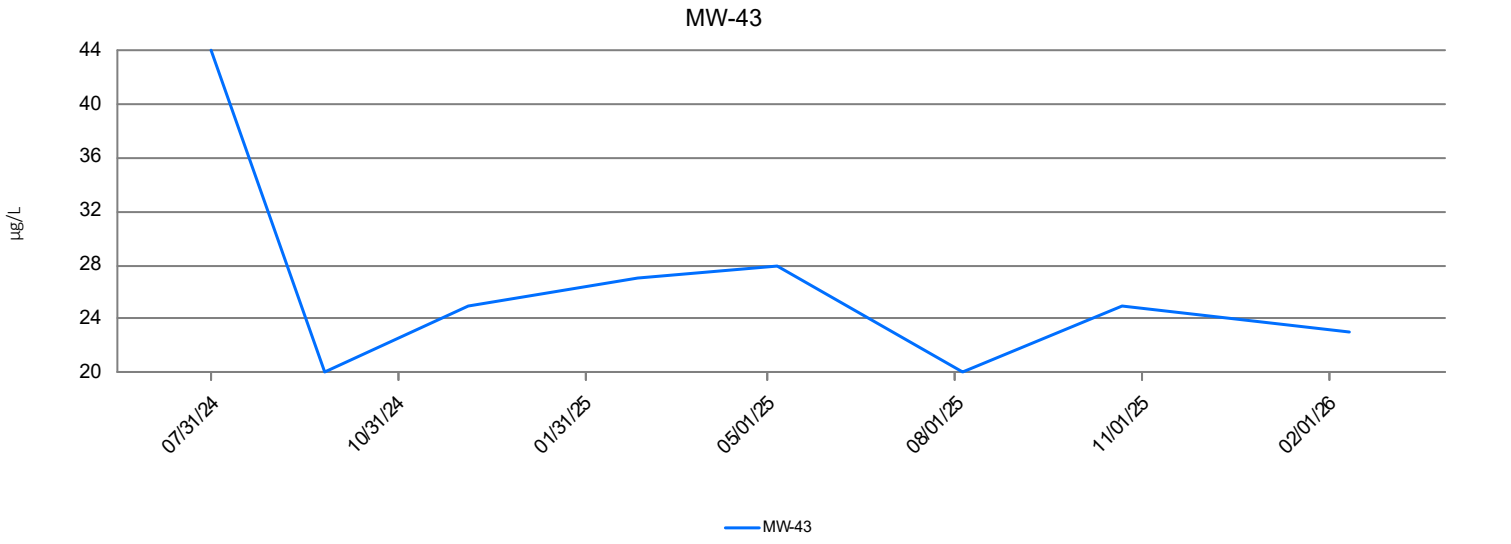


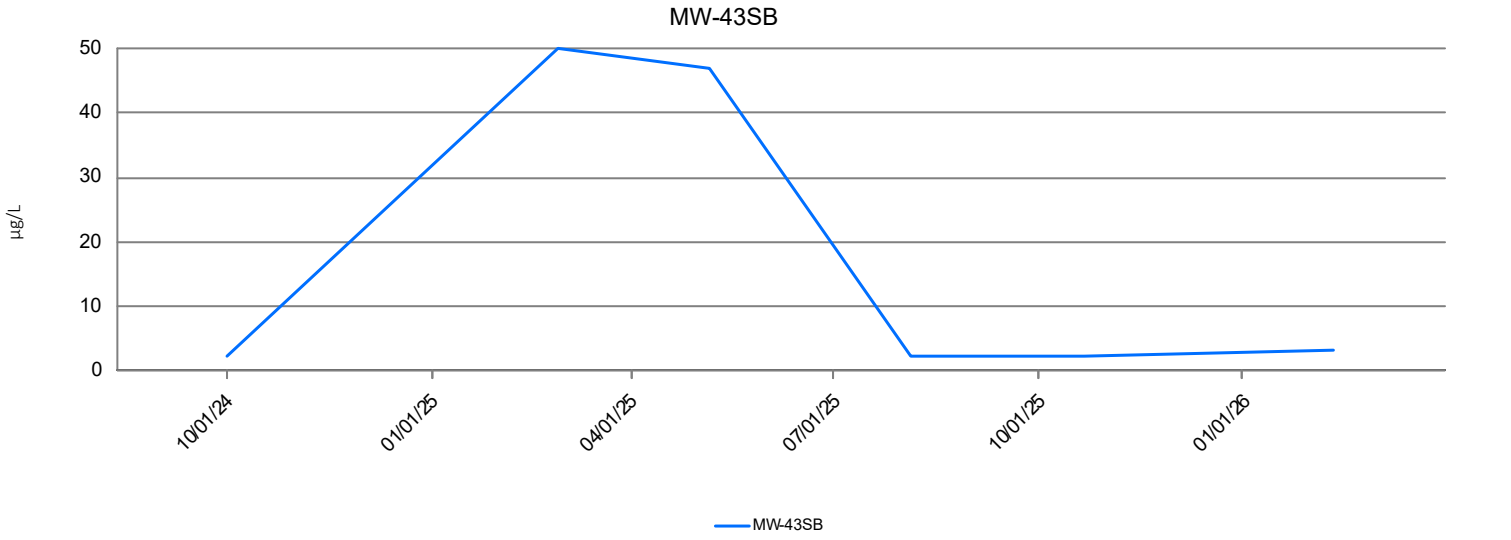
Variable Graphical Report

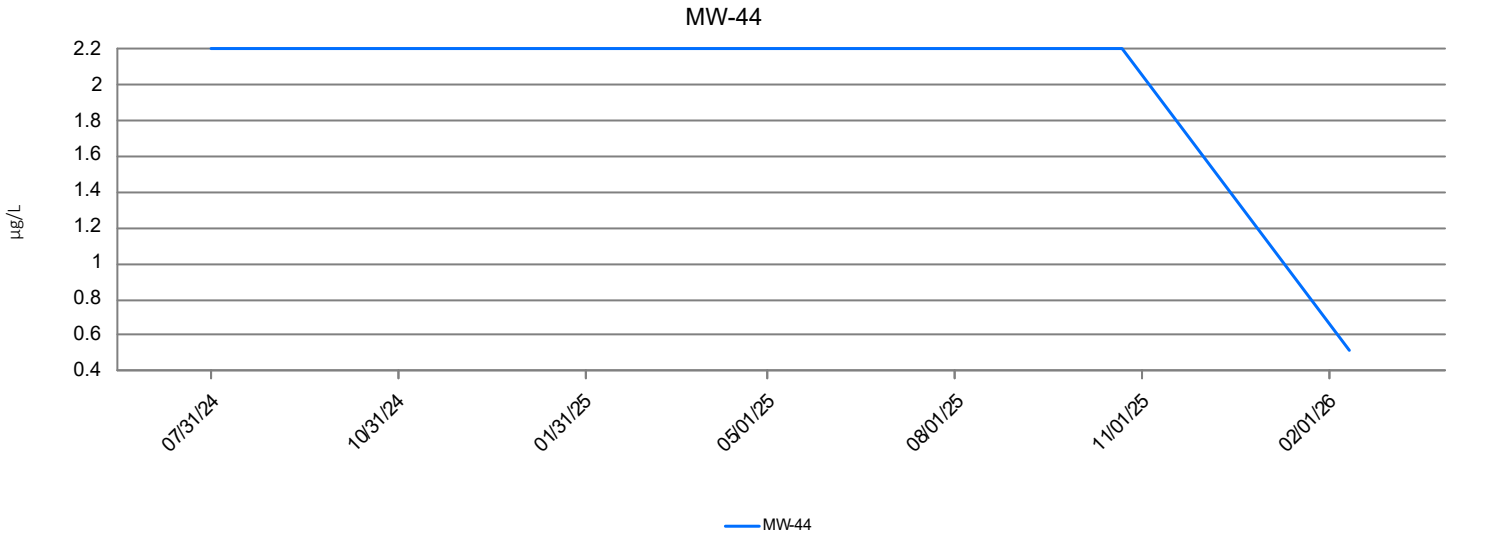
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Vanadium, Total Recoverable (µg/L)





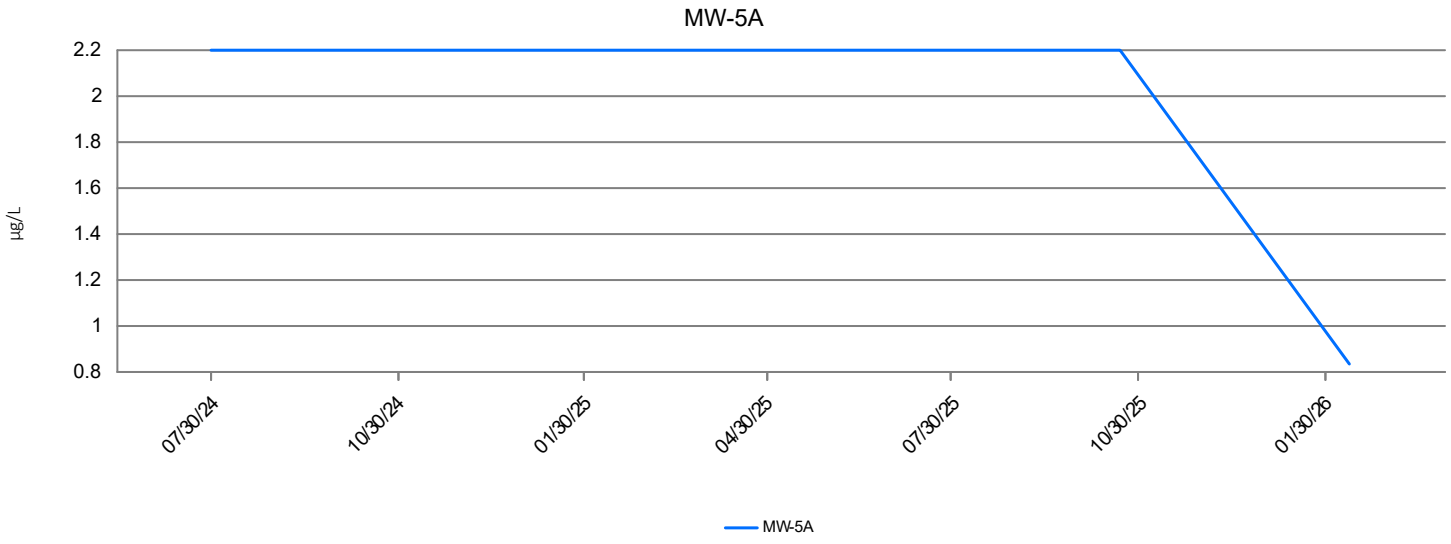


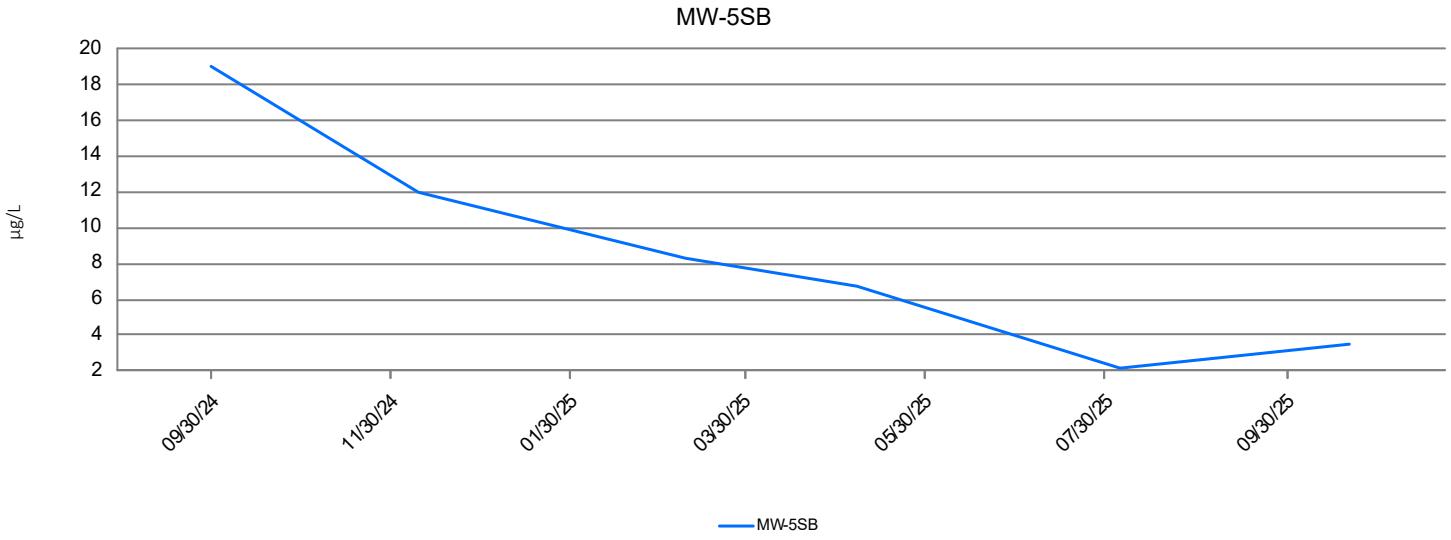
Variable Graphical Report

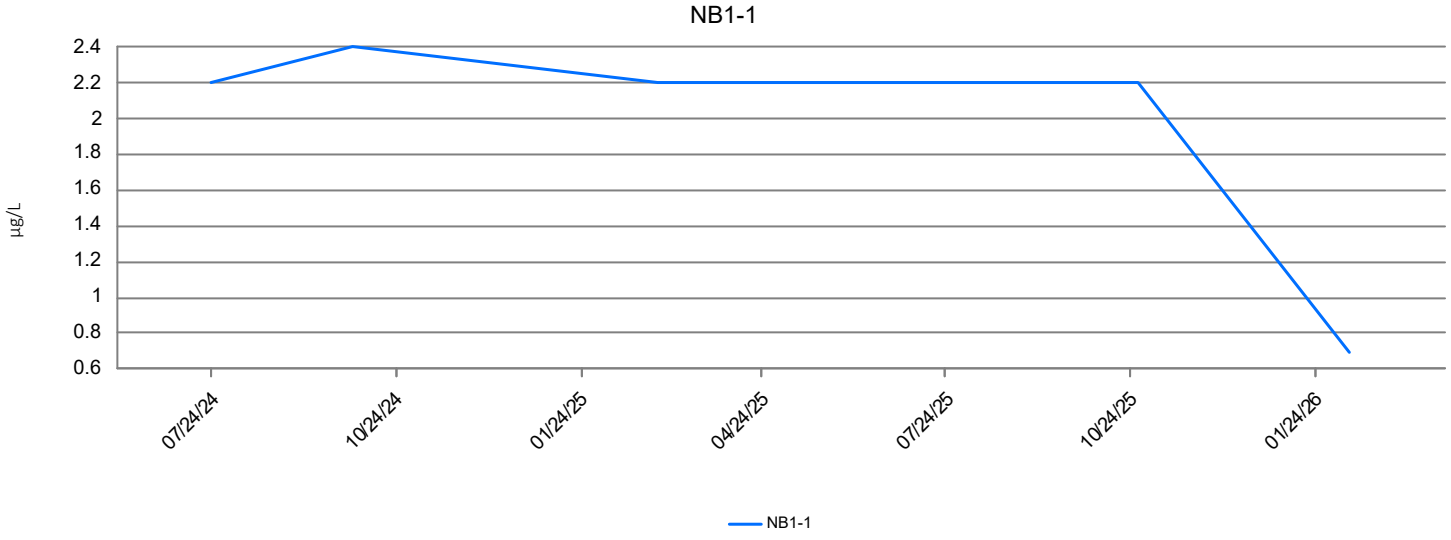
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Vanadium, Total Recoverable (µg/L)





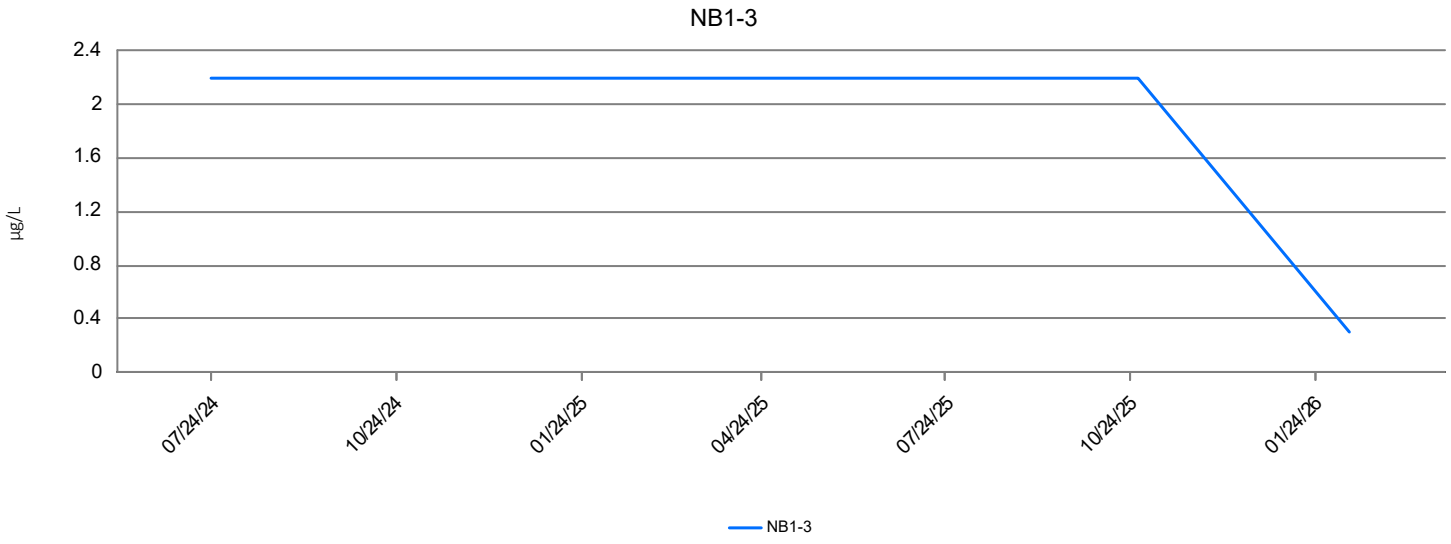


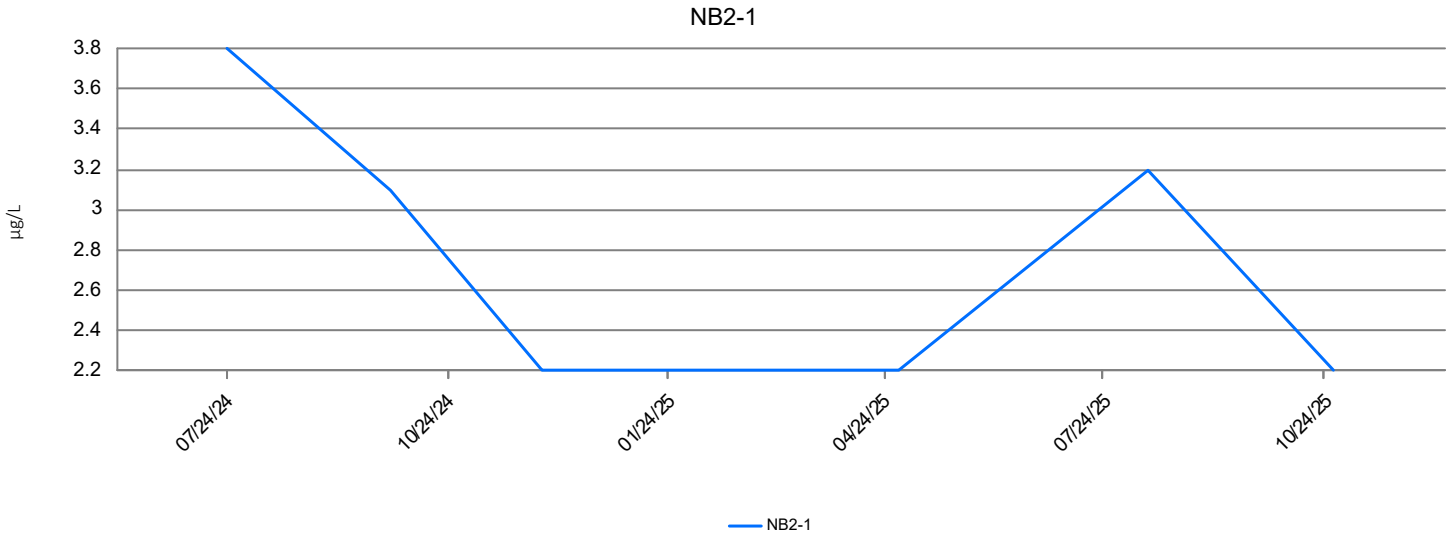
Variable Graphical Report

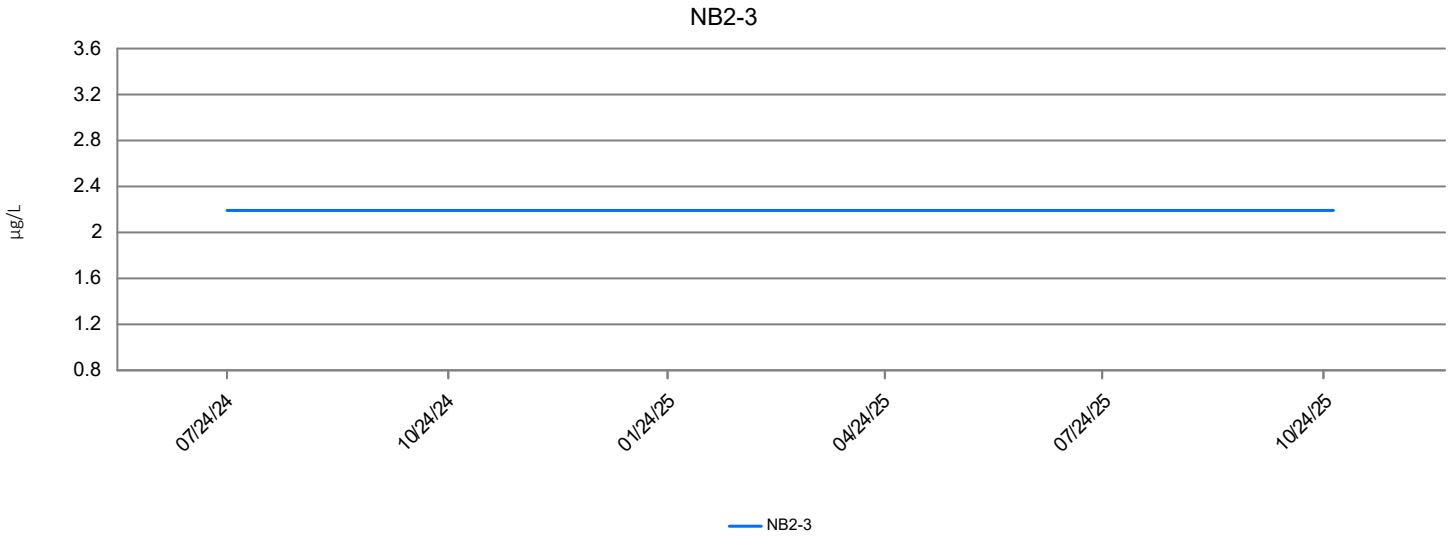
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Vanadium, Total Recoverable (µg/L)







Printed Date: 05/21/2026

EHS DATA

MCERTS Cert. no. Sira MC090140/02

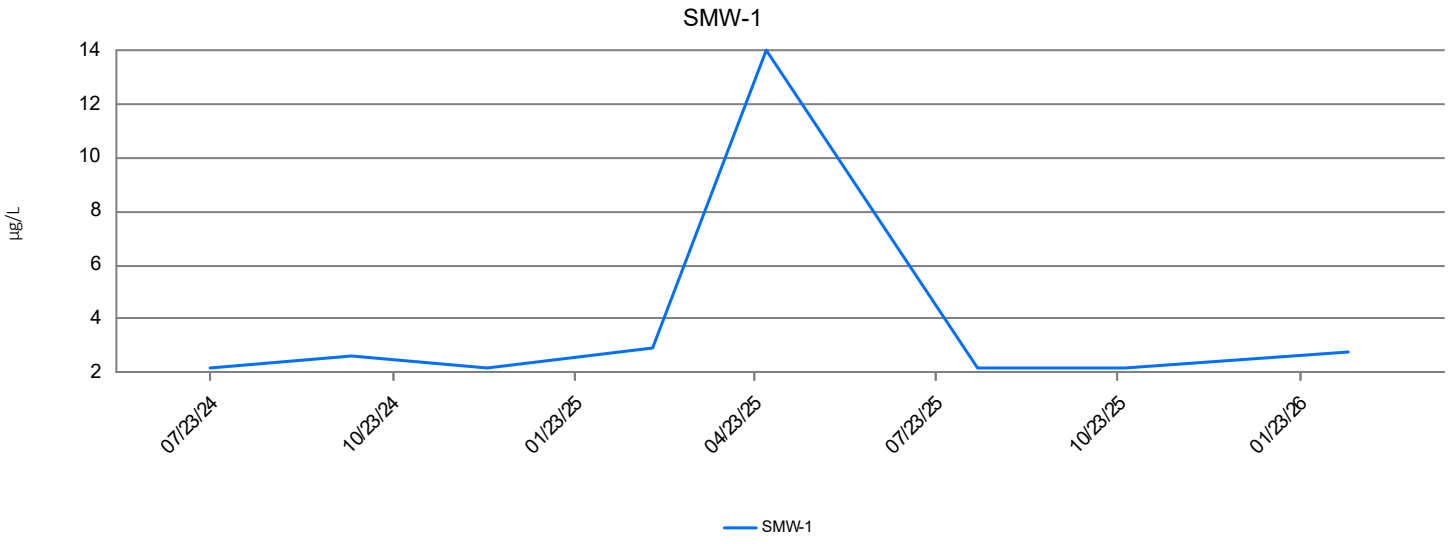
MCERTS

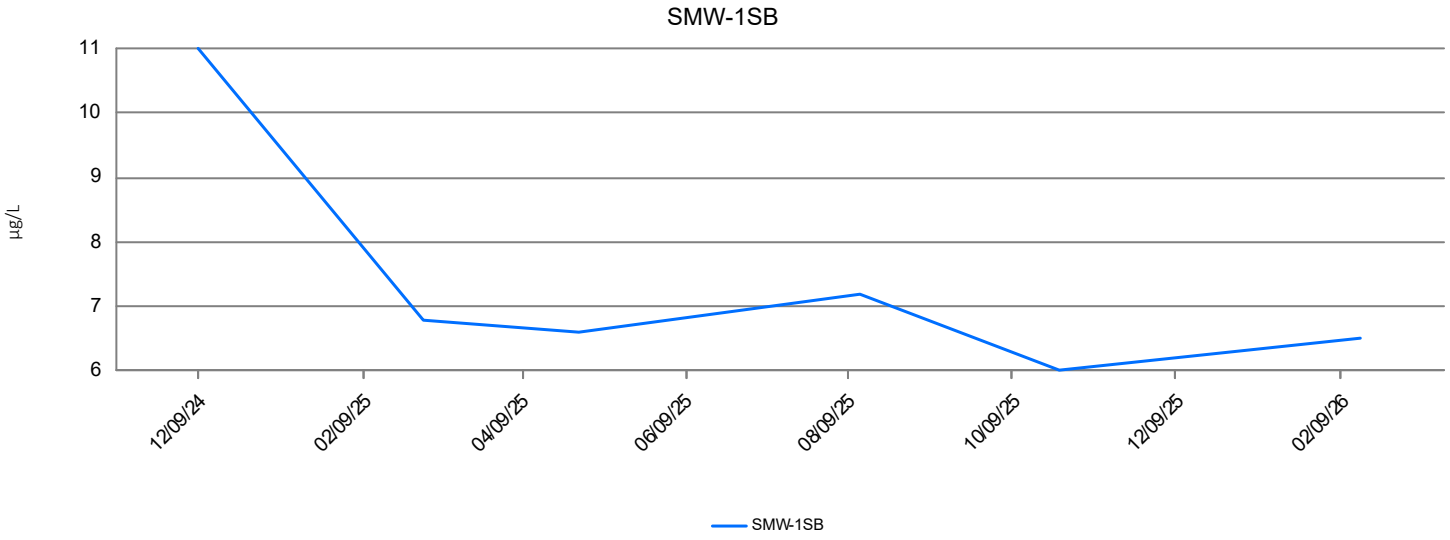
Variable Graphical Report

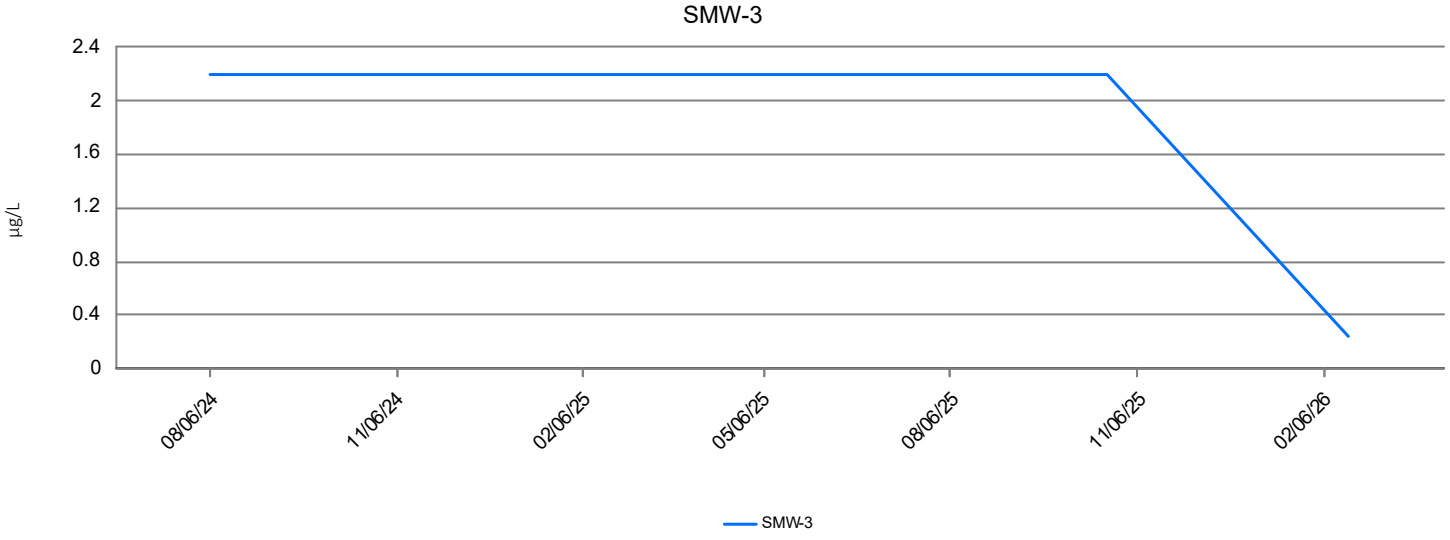
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Vanadium, Total Recoverable (µg/L)





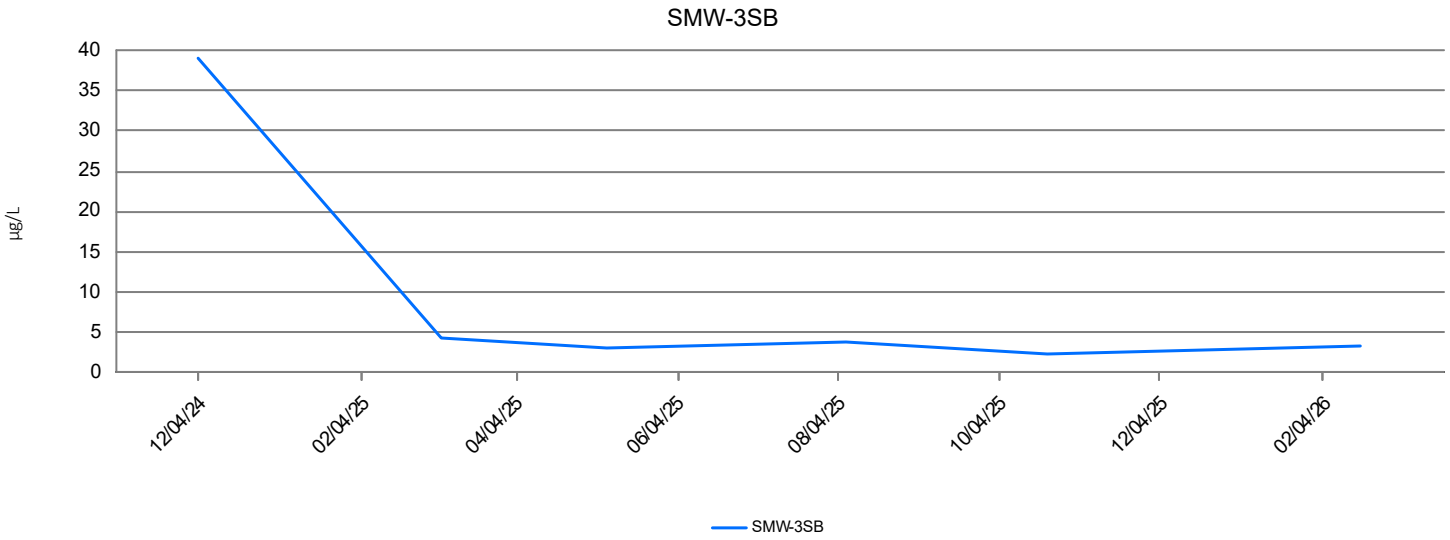


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Vanadium, Total Recoverable (µg/L)

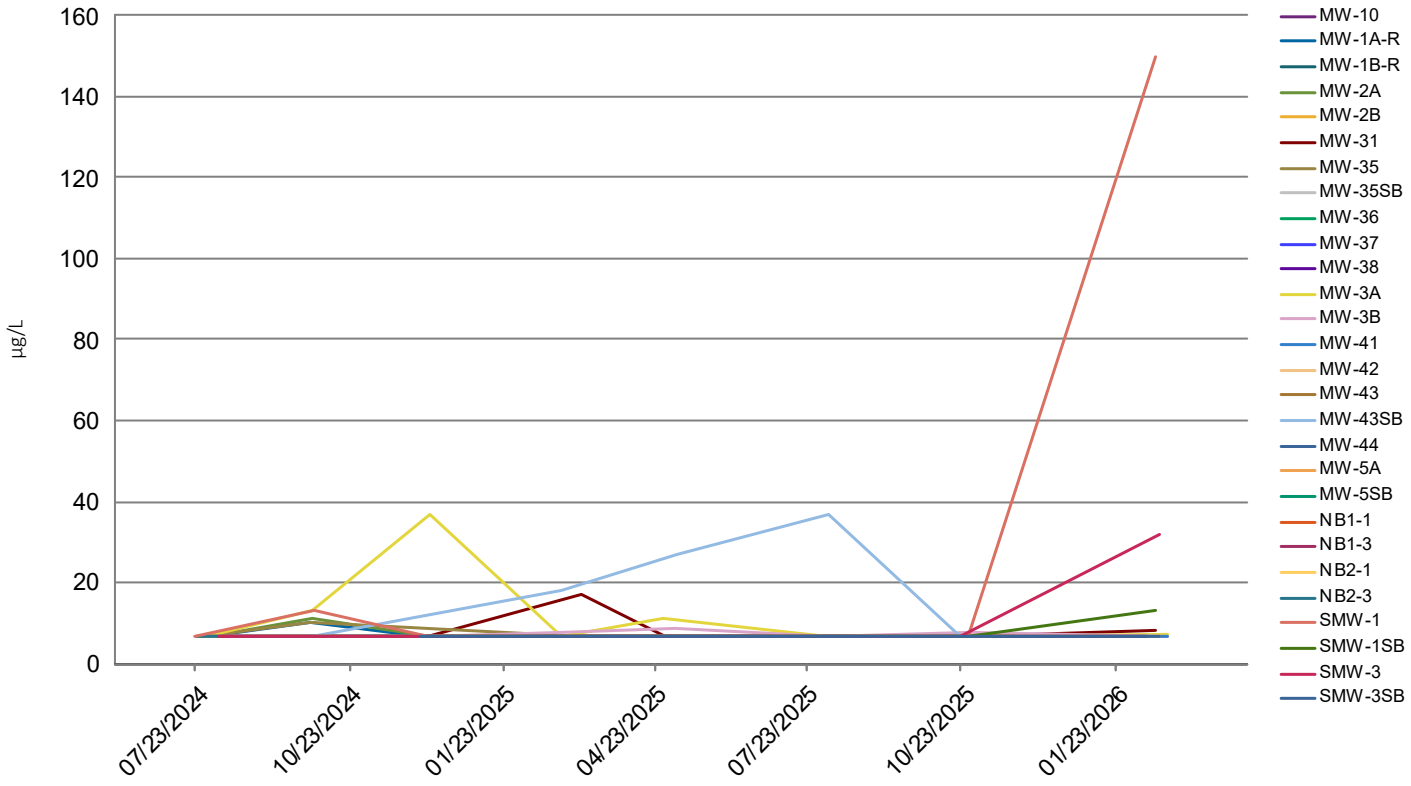


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Zinc, Dissolved (µg/L)



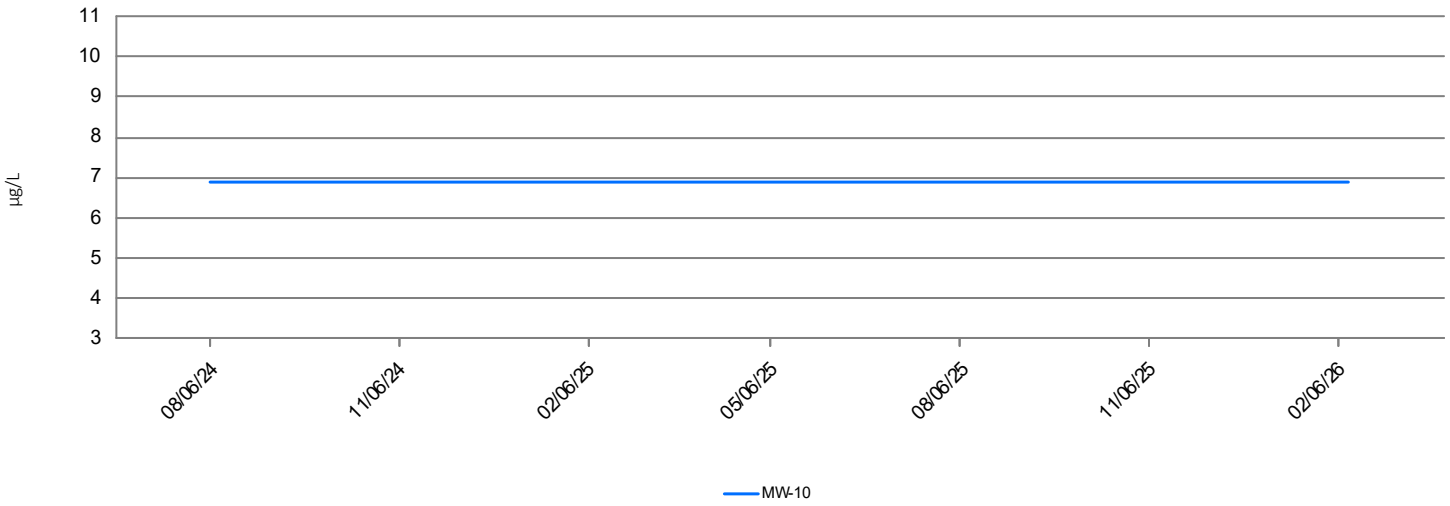
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

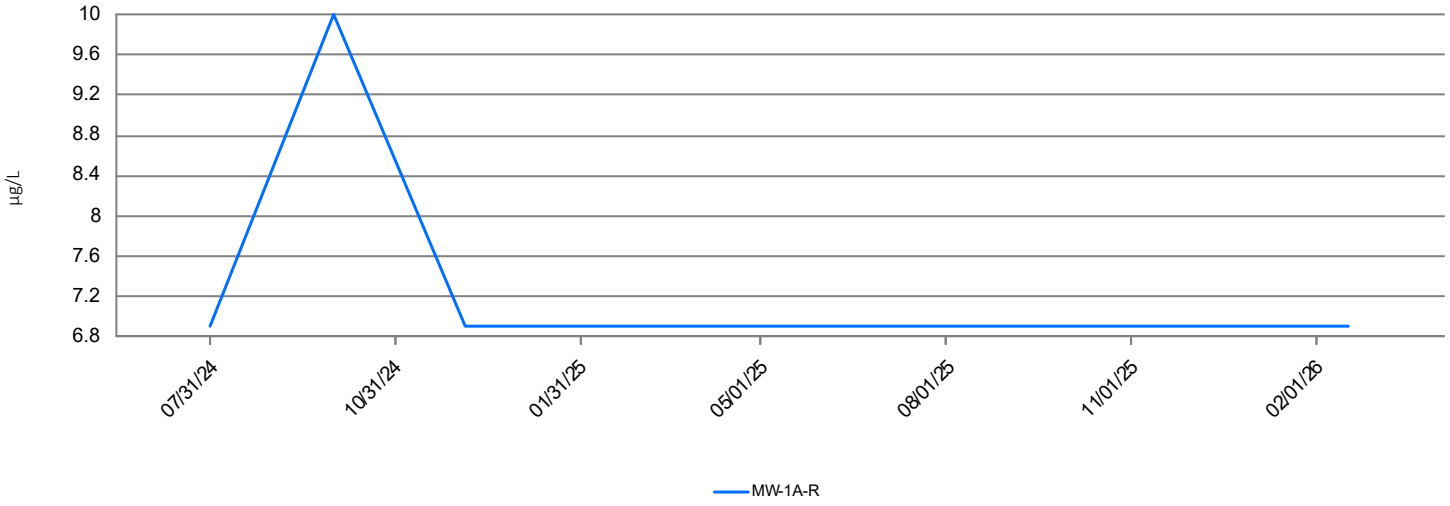
MonitorPro

No Group Selected, Zinc, Dissolved (µg/L)

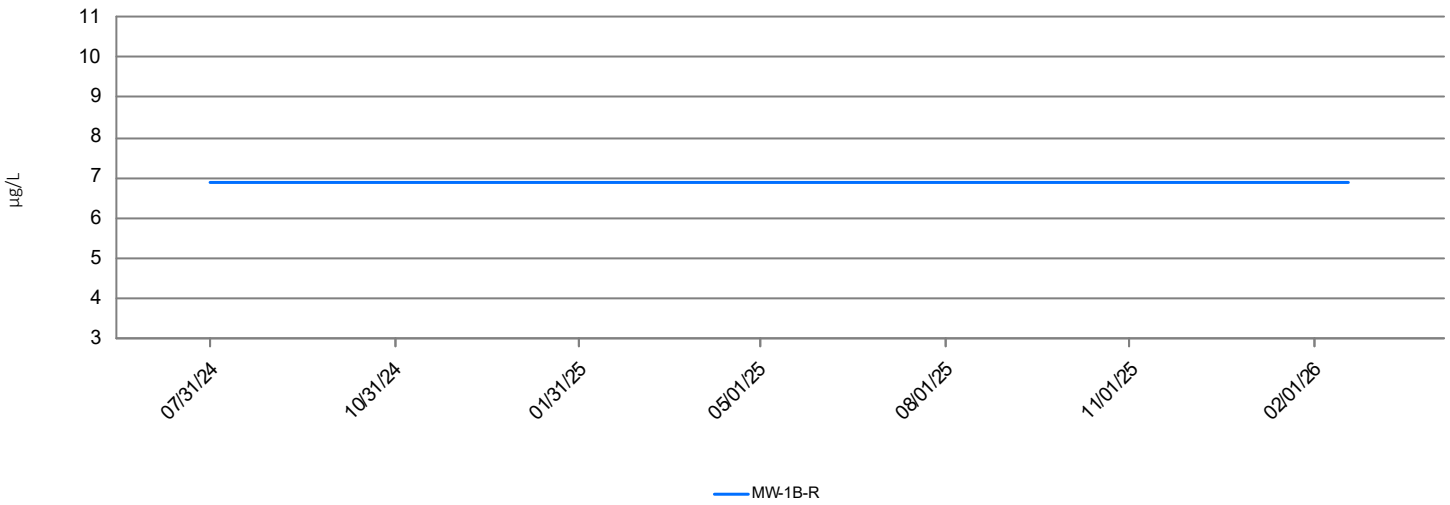
MW-10



MW-1A-R



MW-1B-R



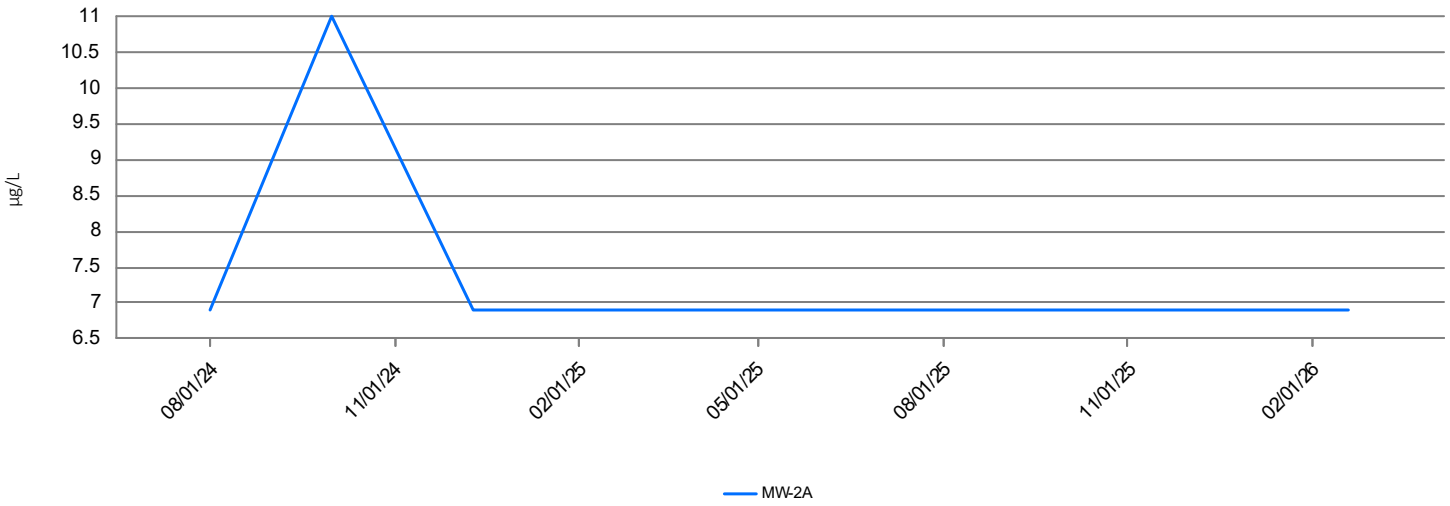
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

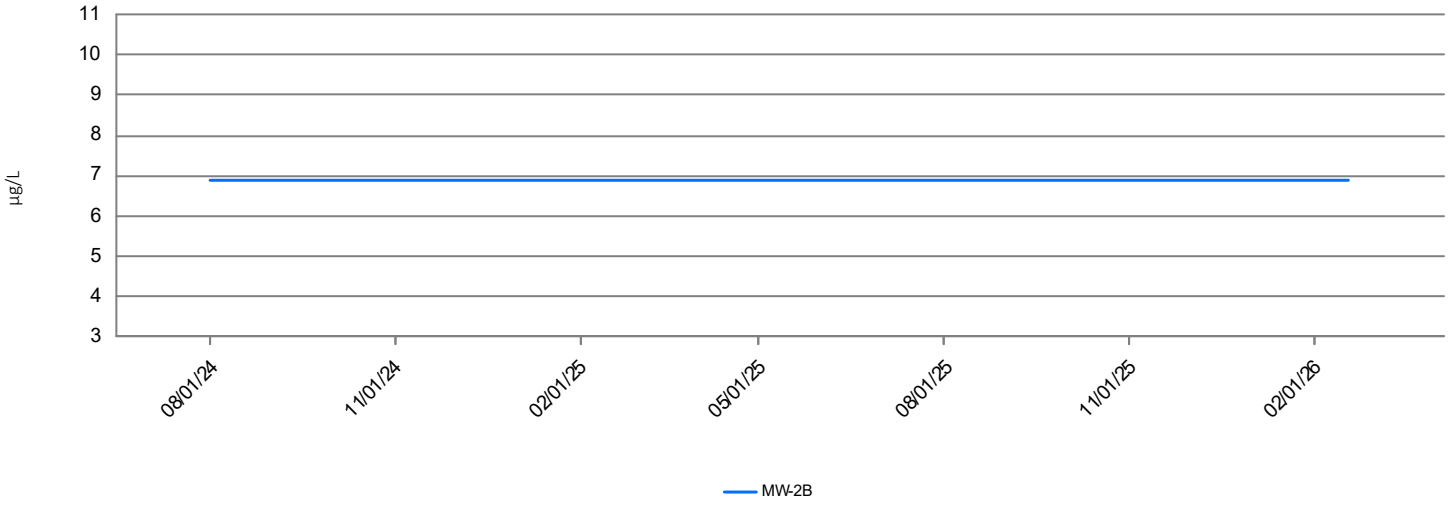
MonitorPro

No Group Selected, Zinc, Dissolved (µg/L)

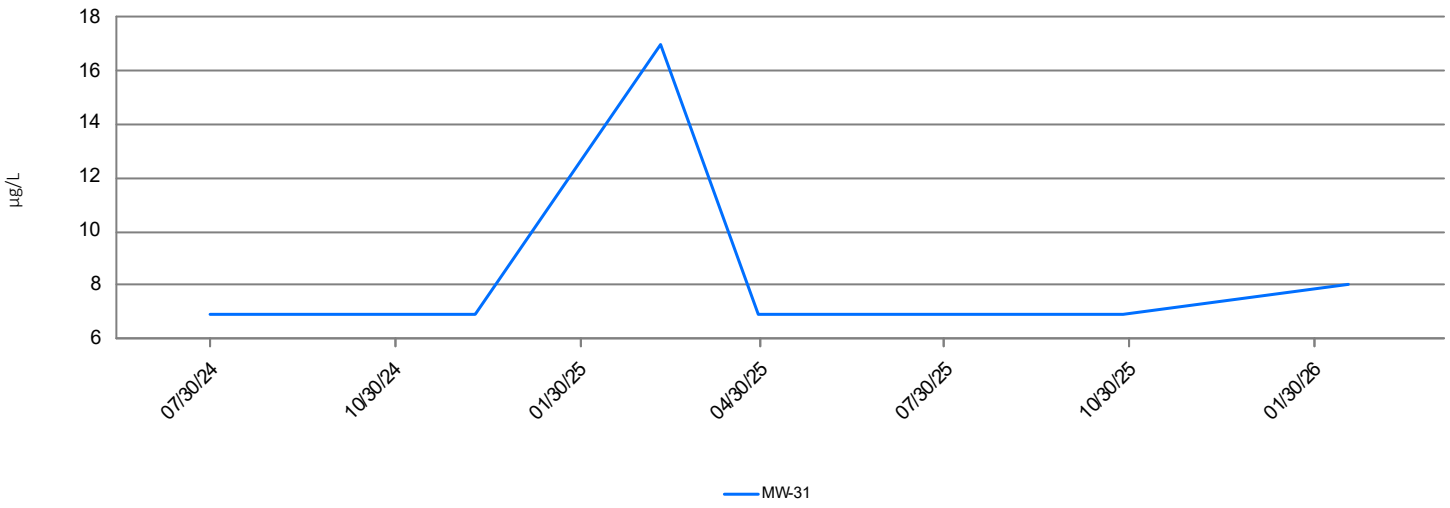
MW-2A



MW-2B



MW-31

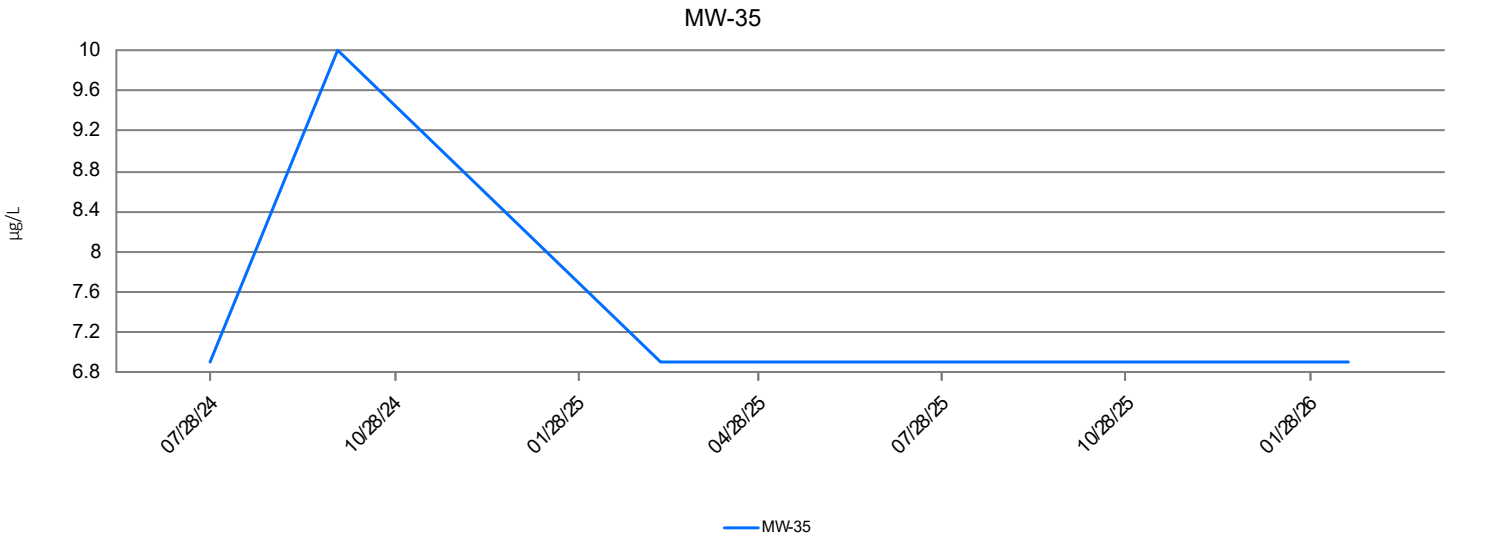


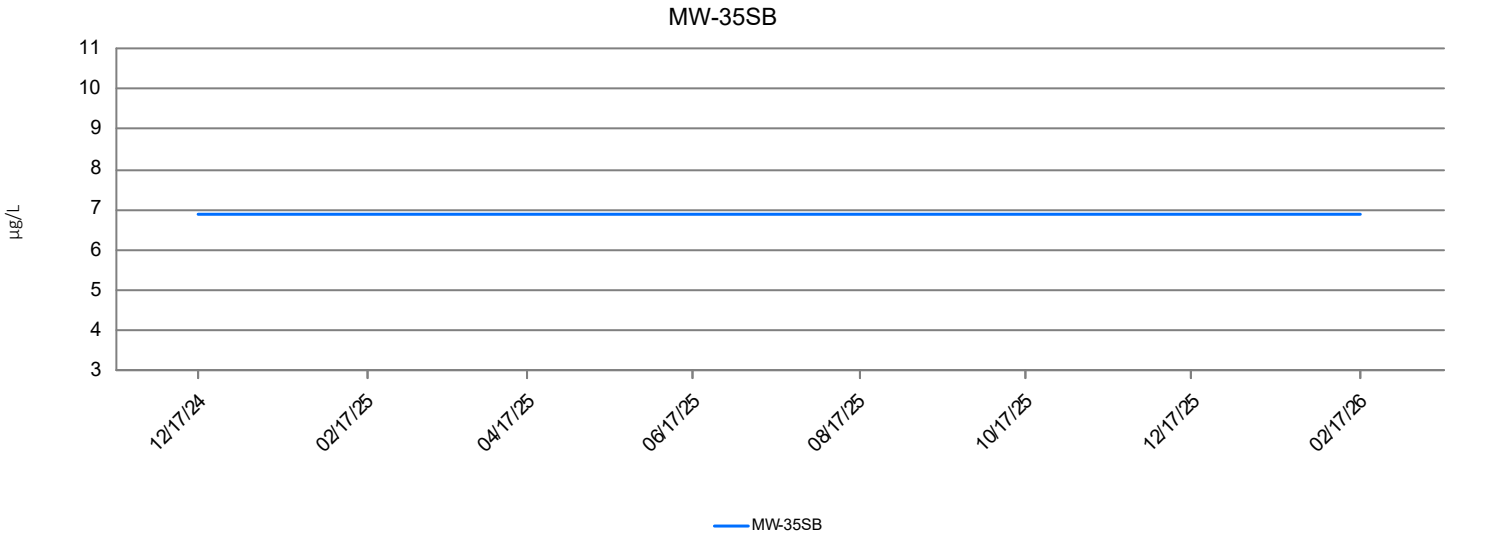
Variable Graphical Report

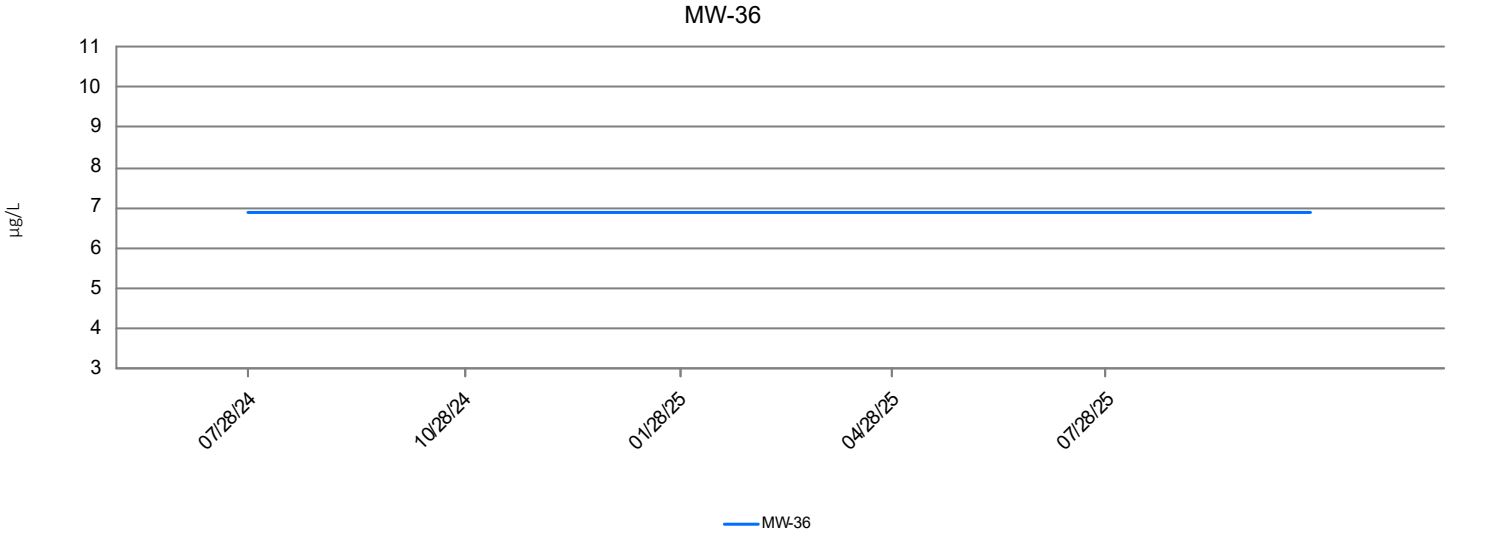
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Zinc, Dissolved (µg/L)







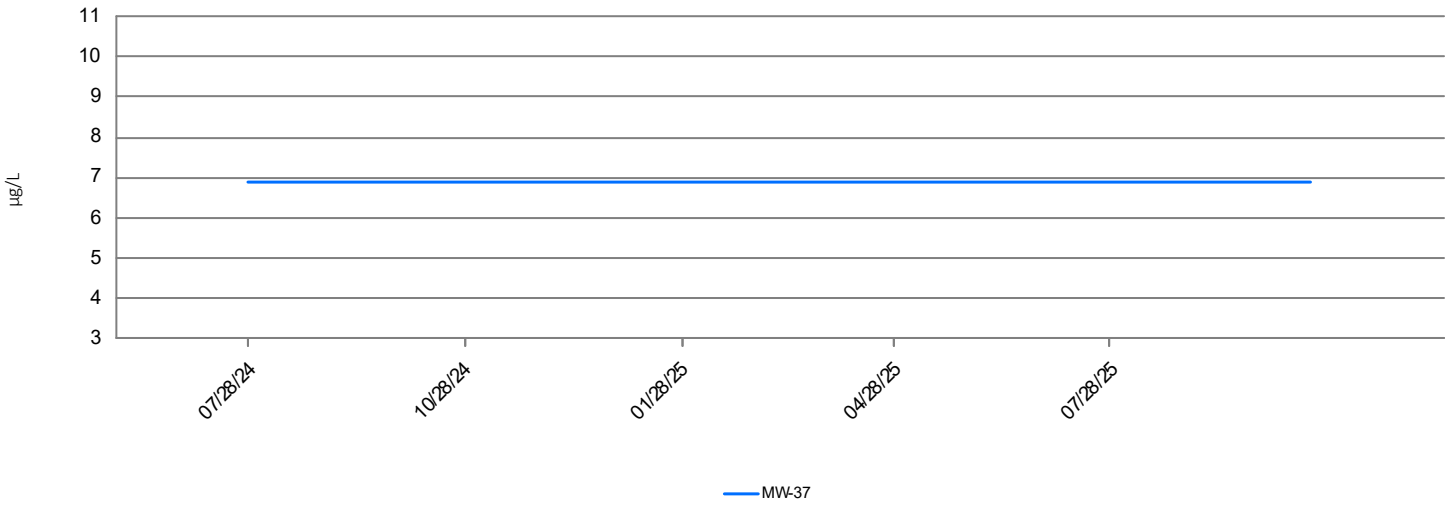
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

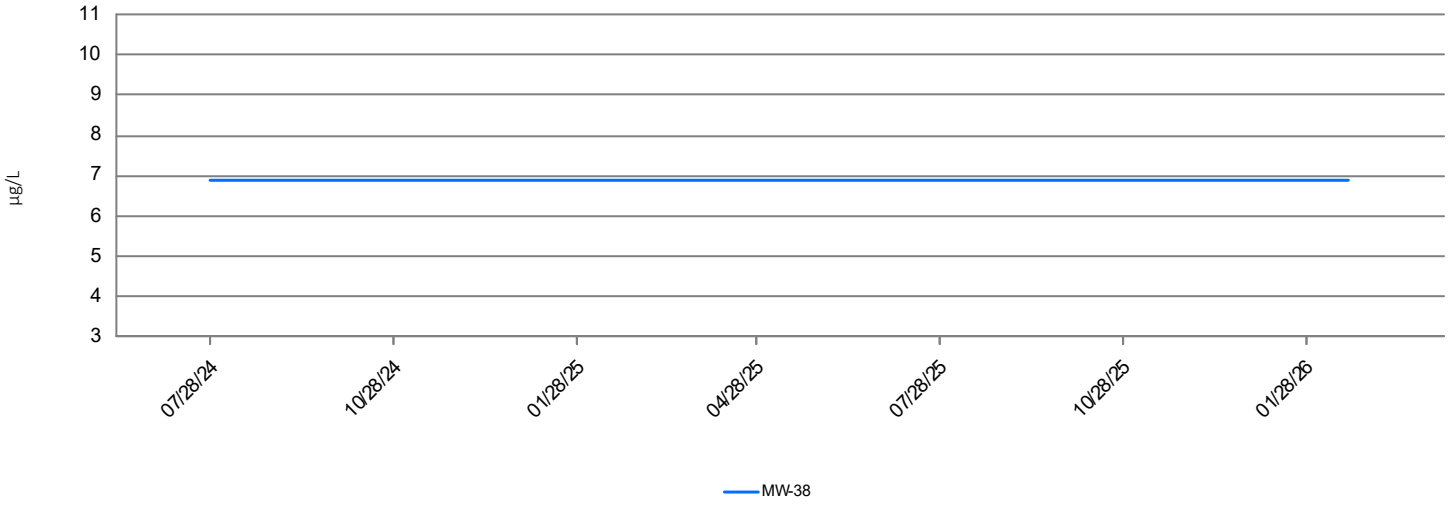
MonitorPro

No Group Selected, Zinc, Dissolved (µg/L)

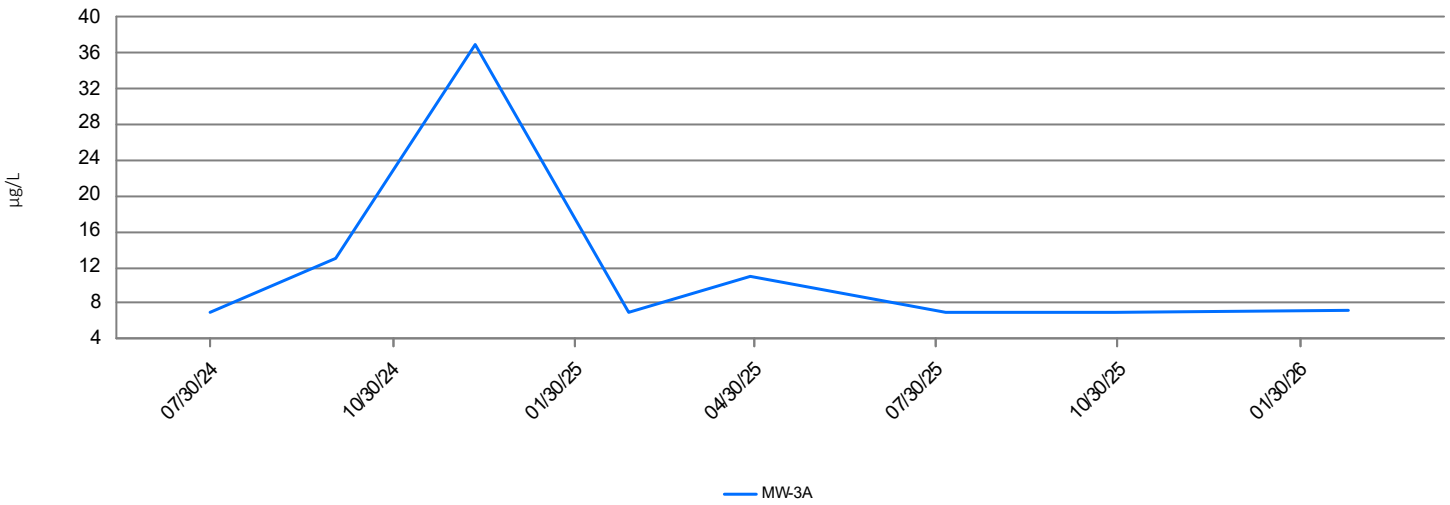
MW-37



MW-38



MW-3A



Printed Date: 05/21/2026

EHS DATA

MCERTS Cert. no. Sira MC090140/02

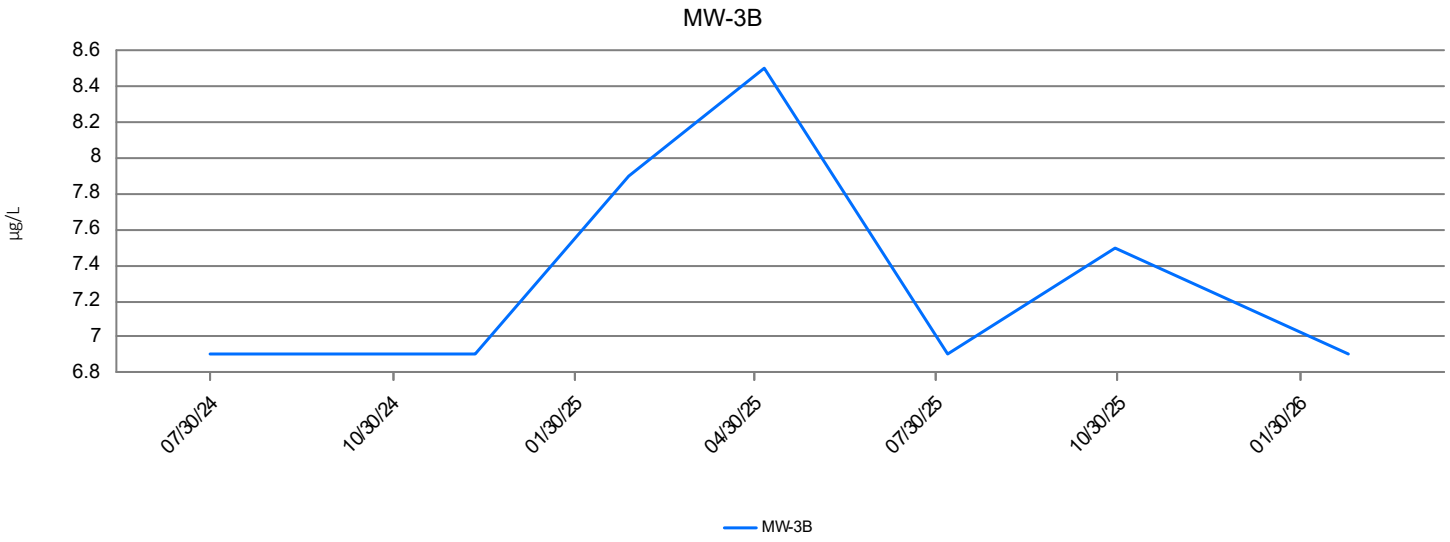
MCERTS

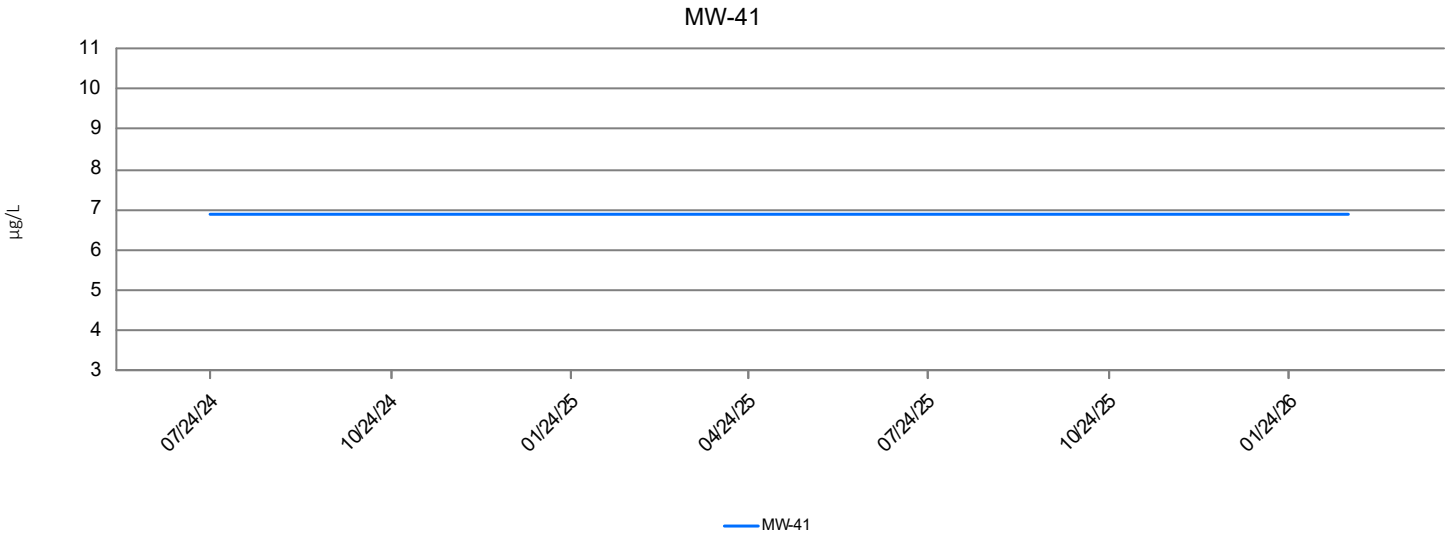
Variable Graphical Report

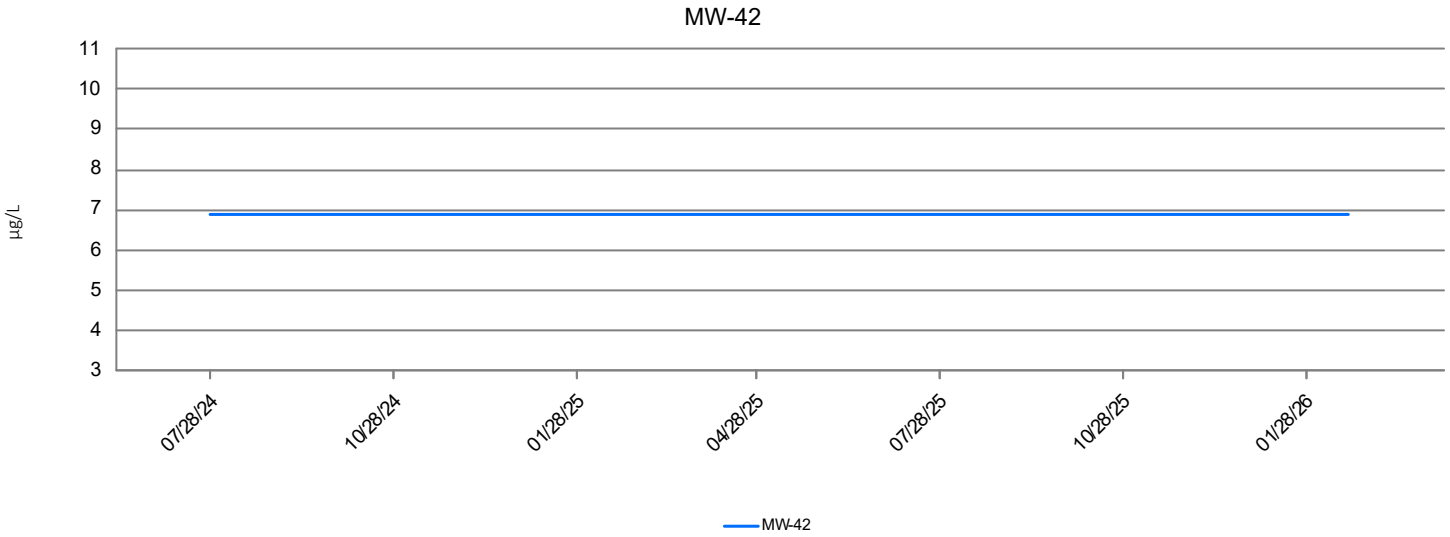
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Zinc, Dissolved (µg/L)







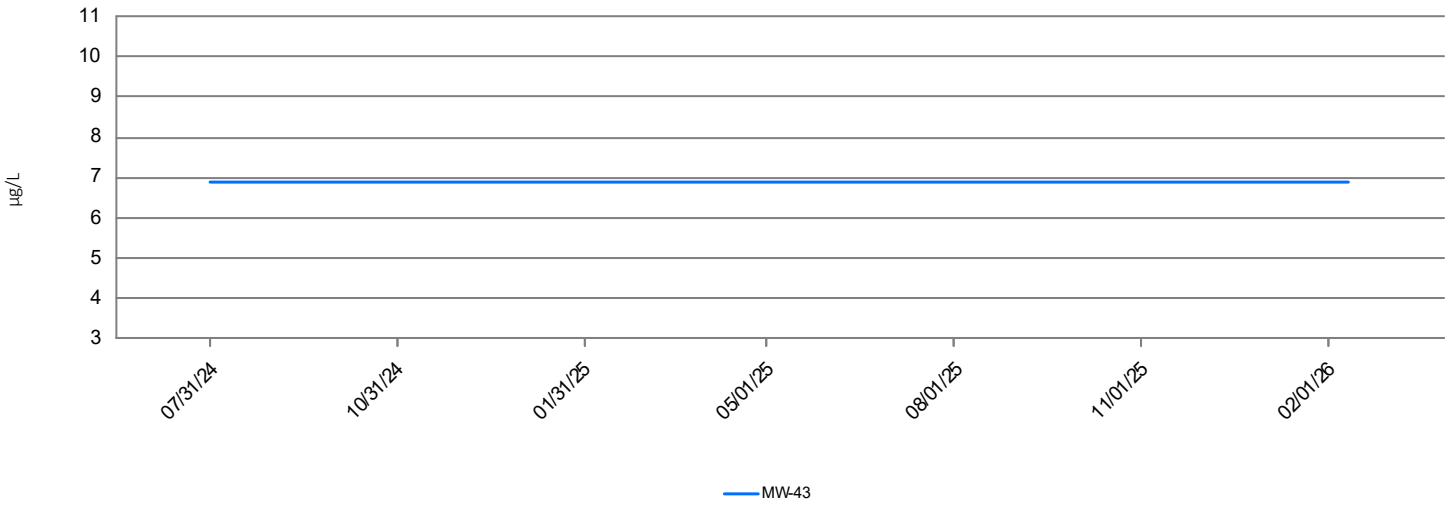
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

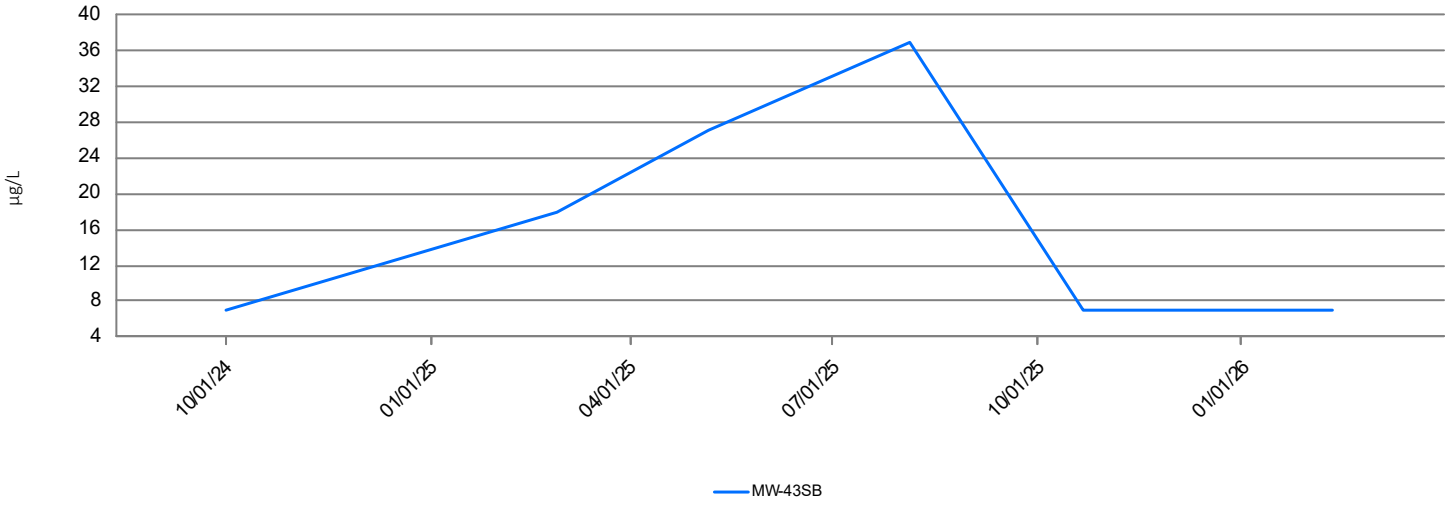
MonitorPro

No Group Selected, Zinc, Dissolved (µg/L)

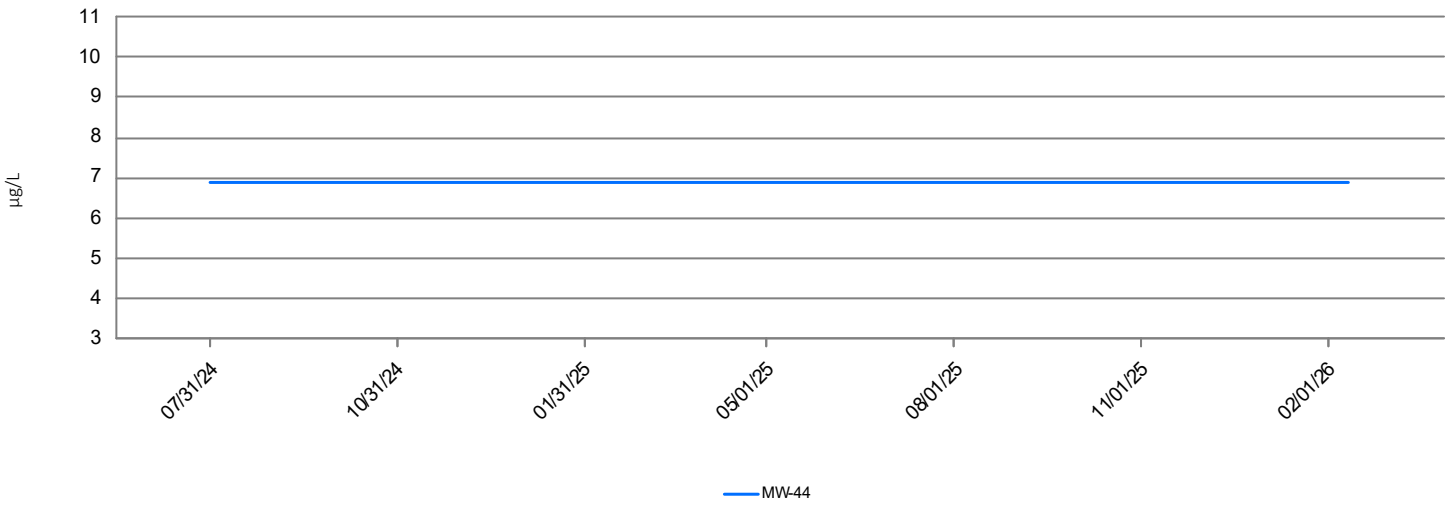
MW-43



MW-43SB



MW-44



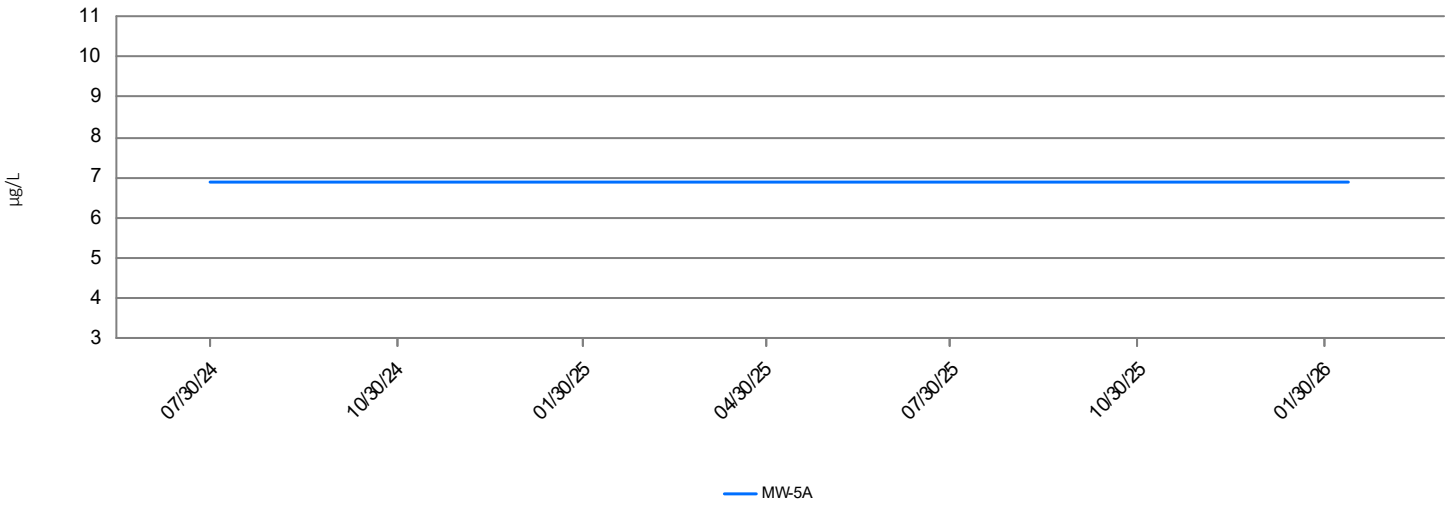
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

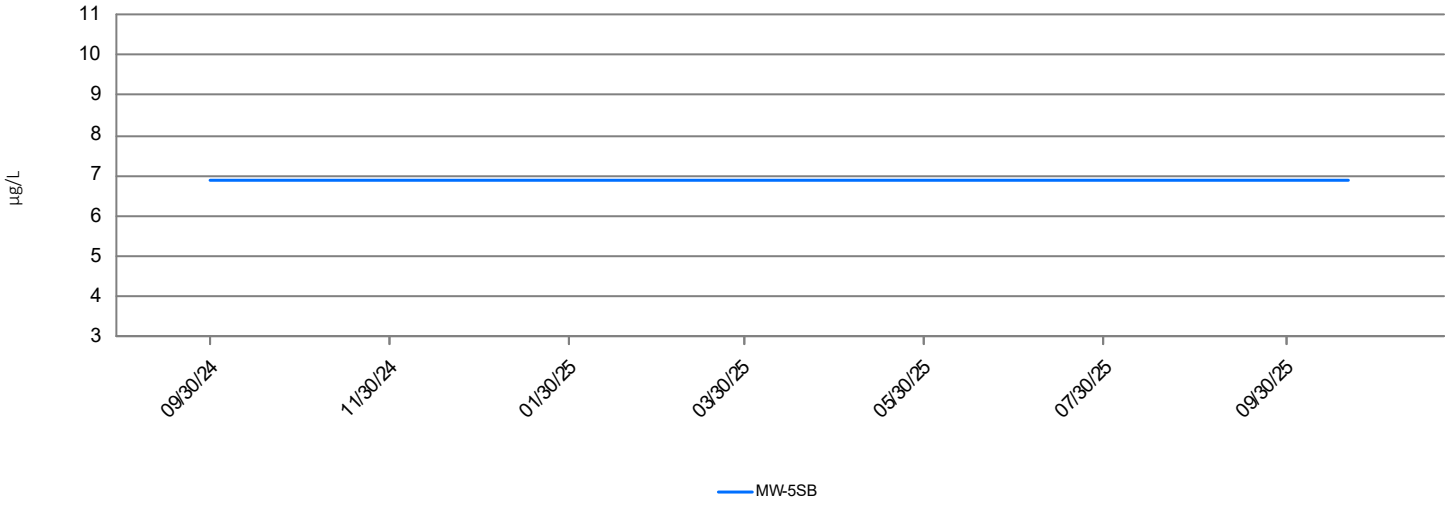
MonitorPro

No Group Selected, Zinc, Dissolved (µg/L)

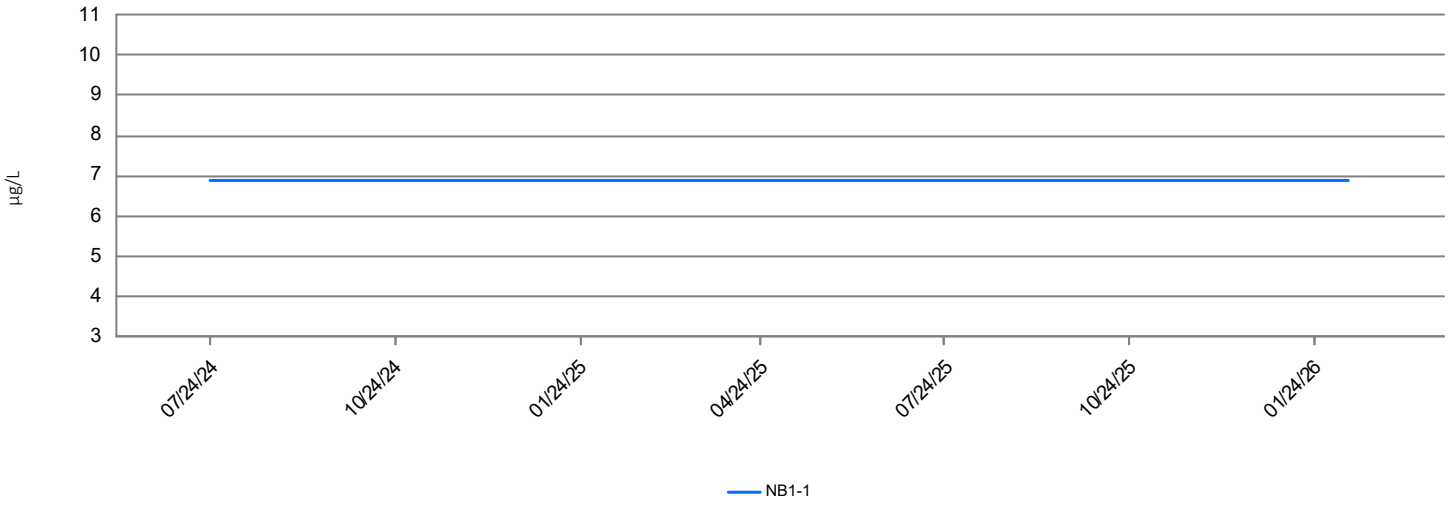
MW-5A



MW-5SB



NB1-1



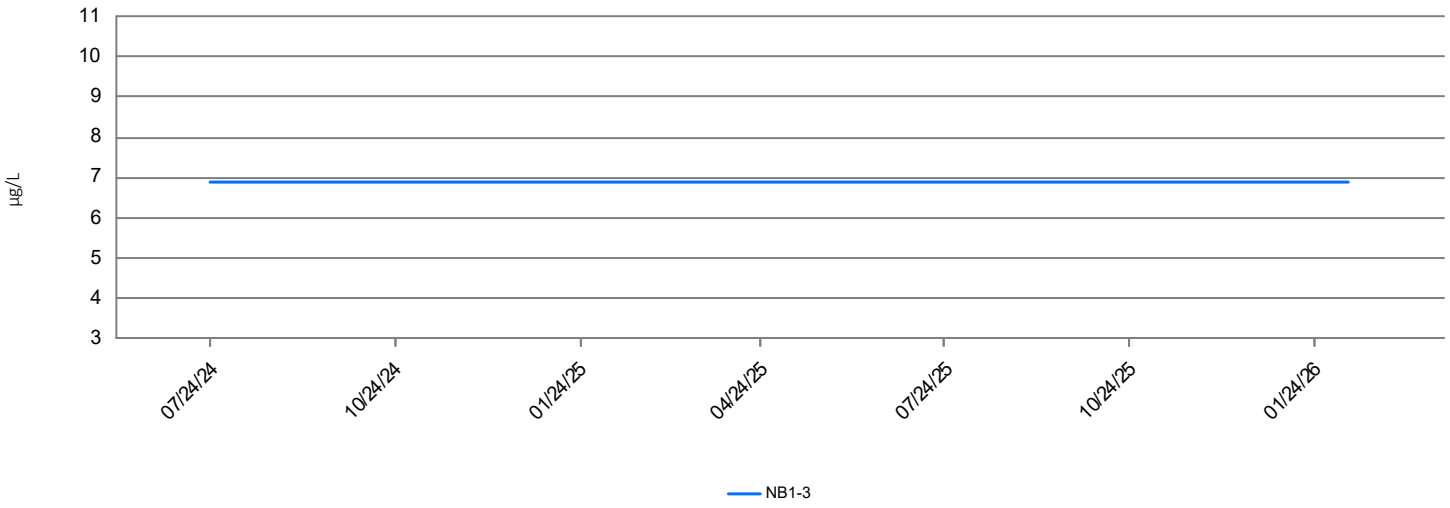
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

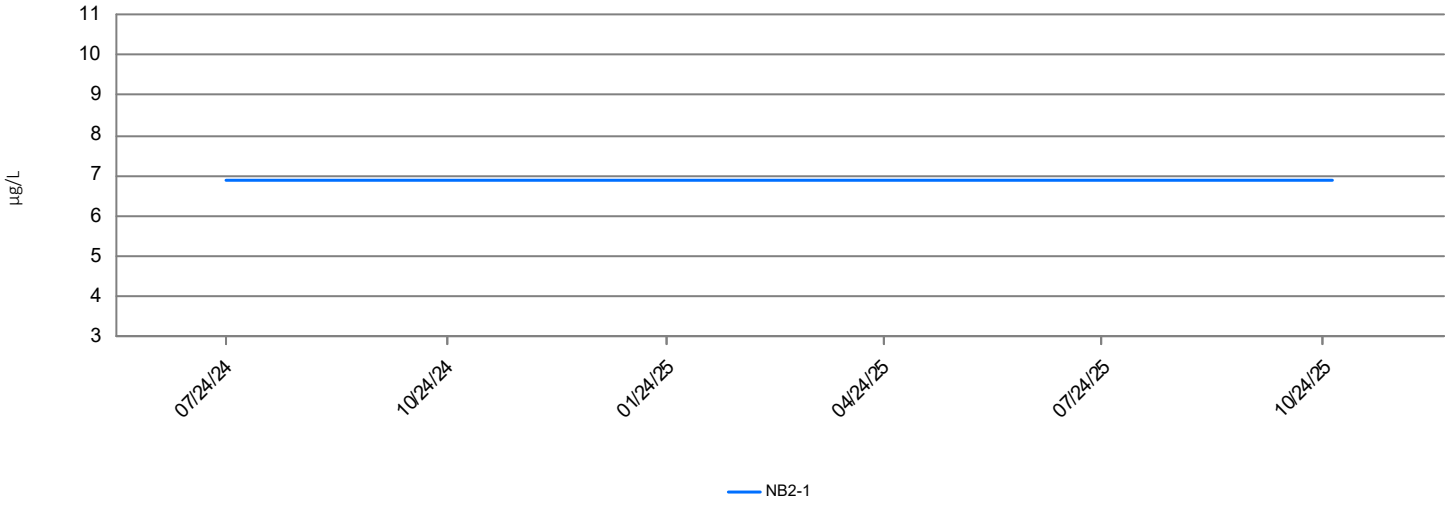
MonitorPro

No Group Selected, Zinc, Dissolved (µg/L)

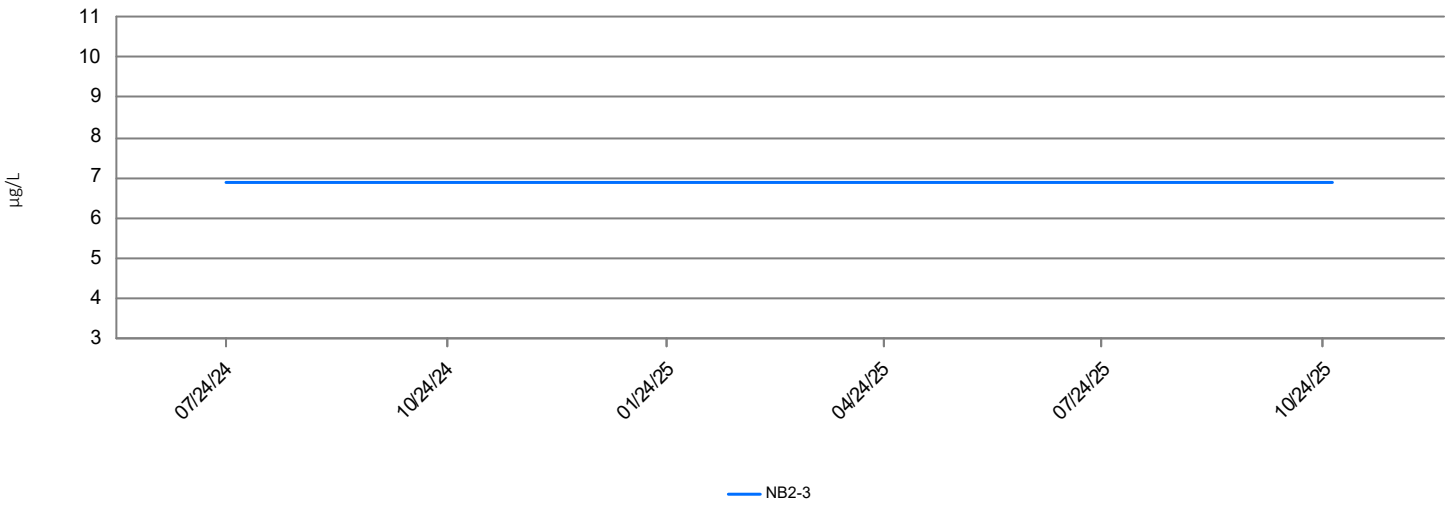
NB1-3



NB2-1



NB2-3



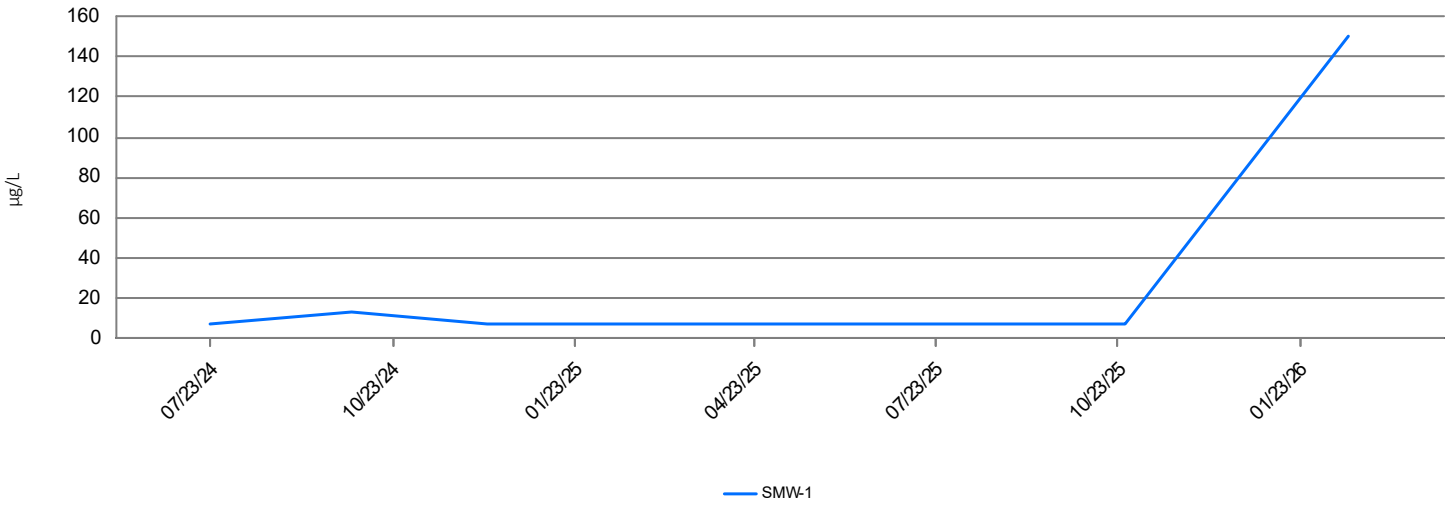
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

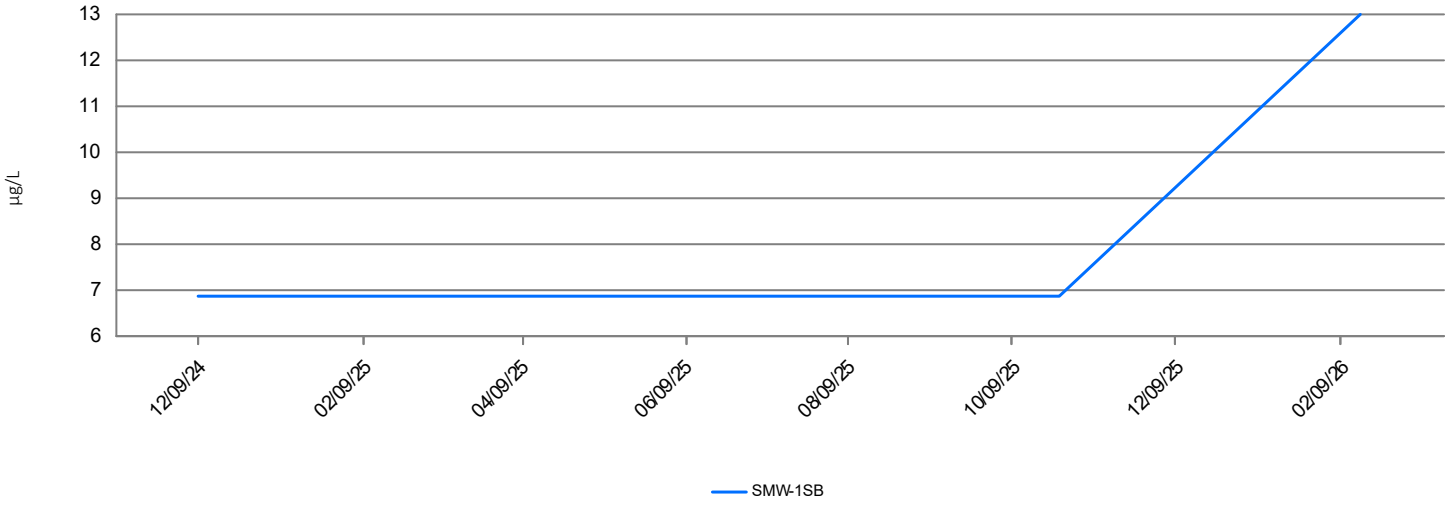
MonitorPro

No Group Selected, Zinc, Dissolved (µg/L)

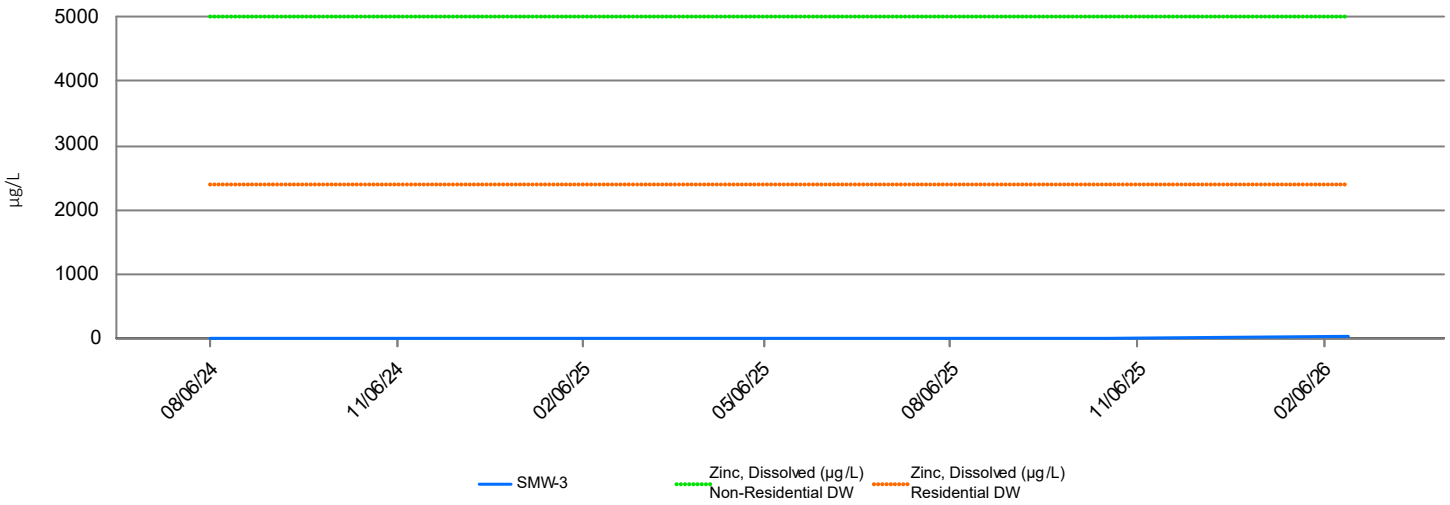
SMW-1



SMW-1SB



SMW-3

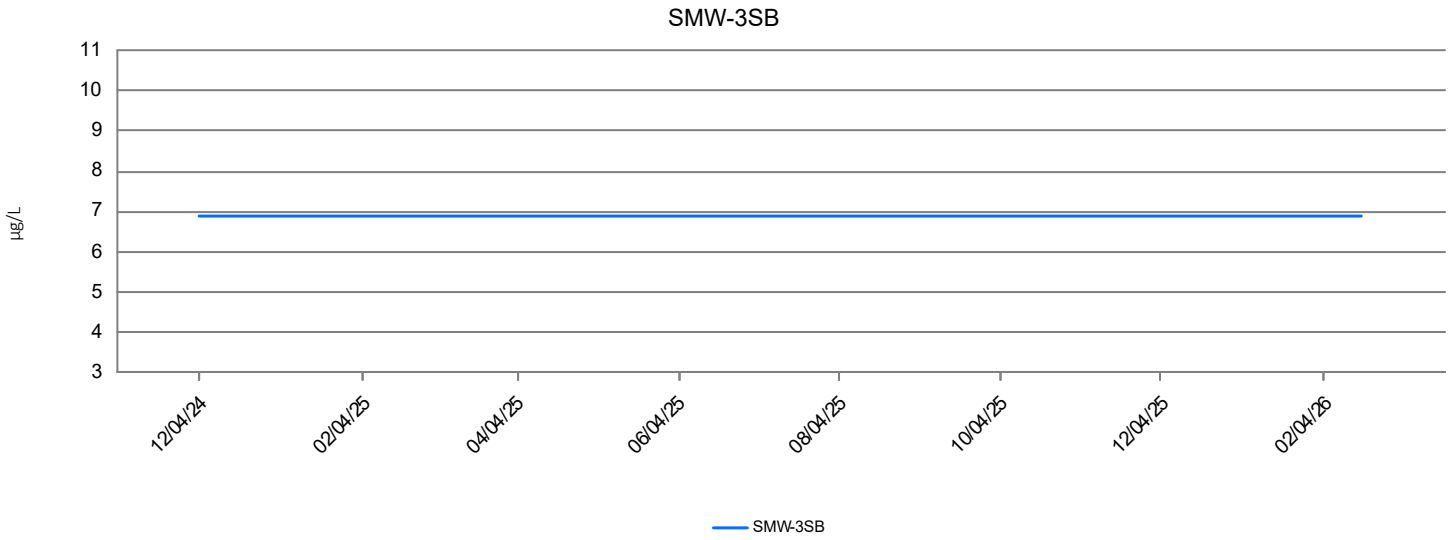


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Zinc, Dissolved (µg/L)

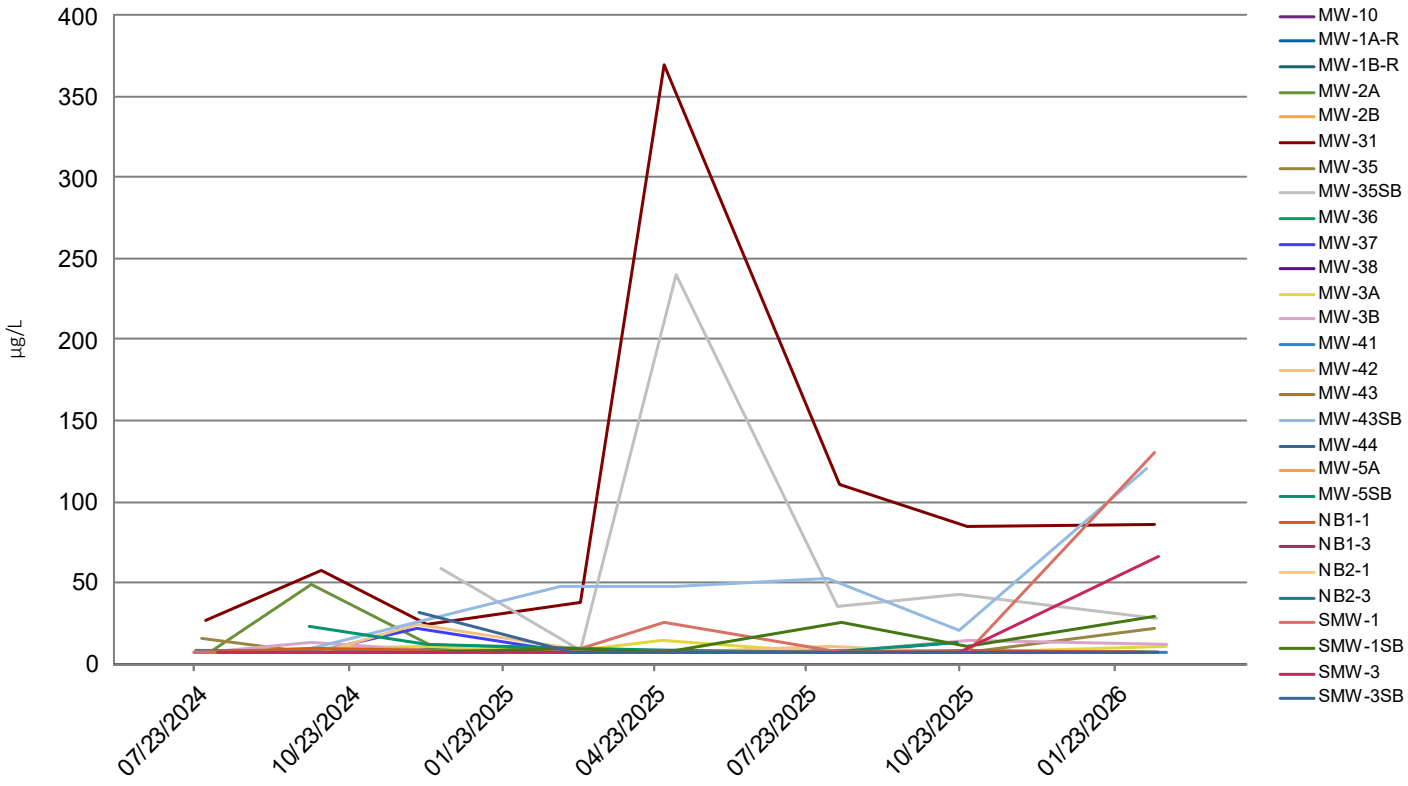


Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Zinc, Total Recoverable (µg/L)

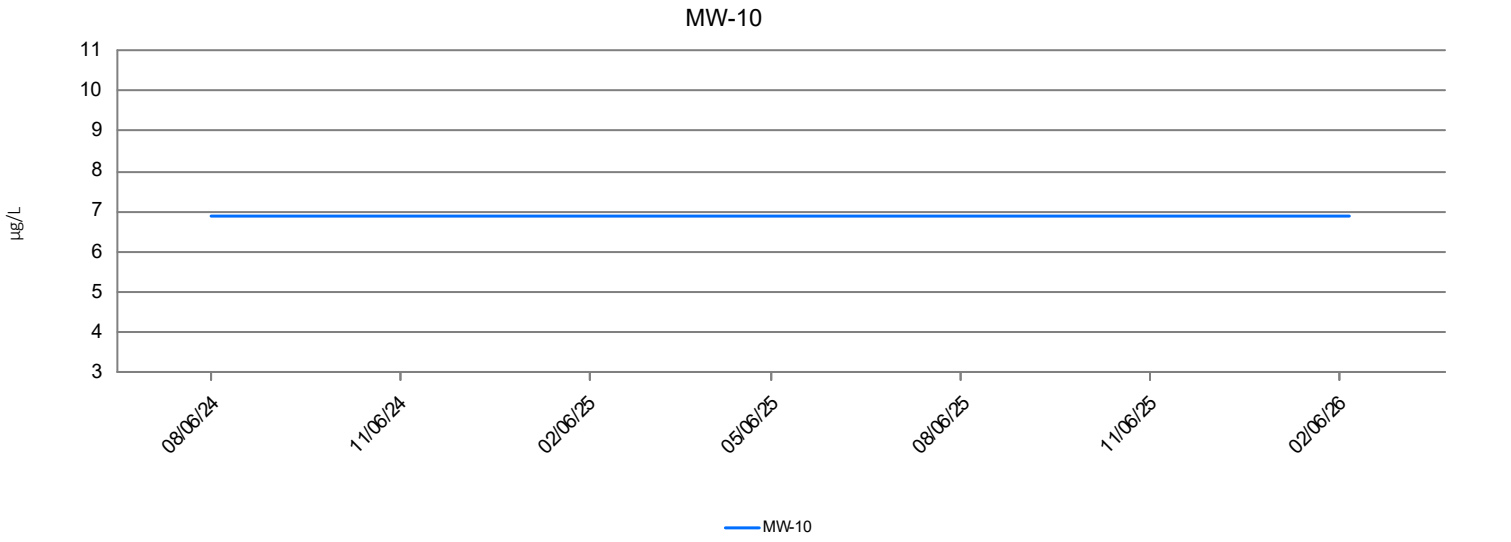


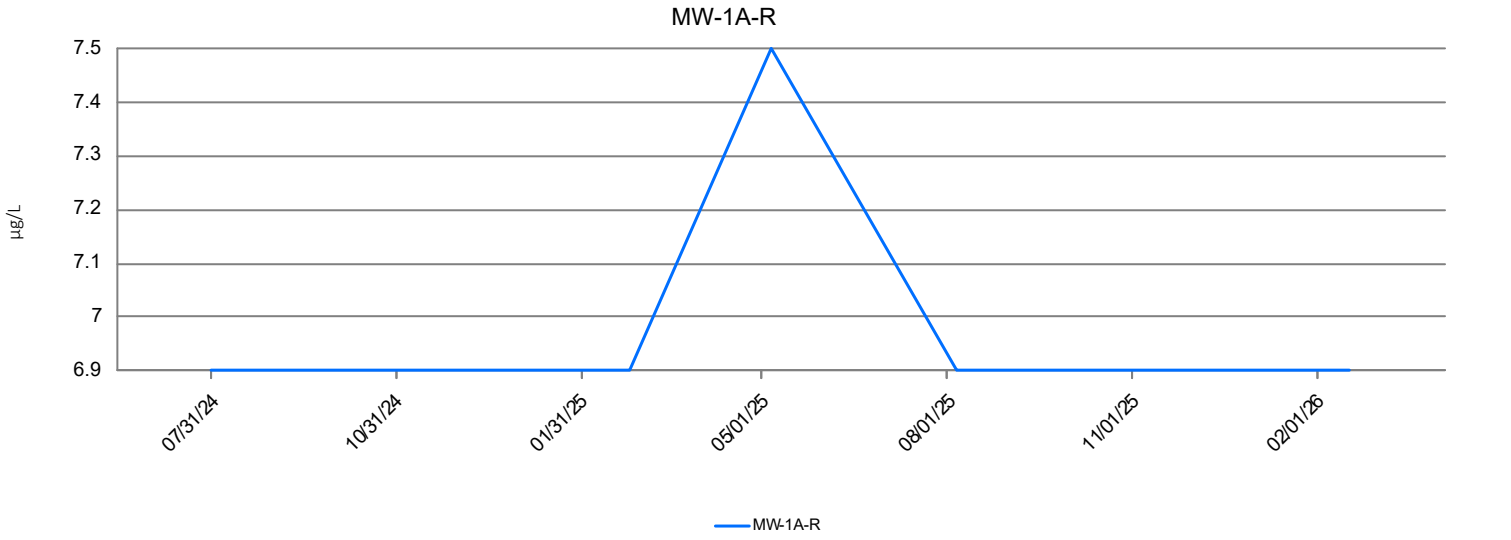
Variable Graphical Report

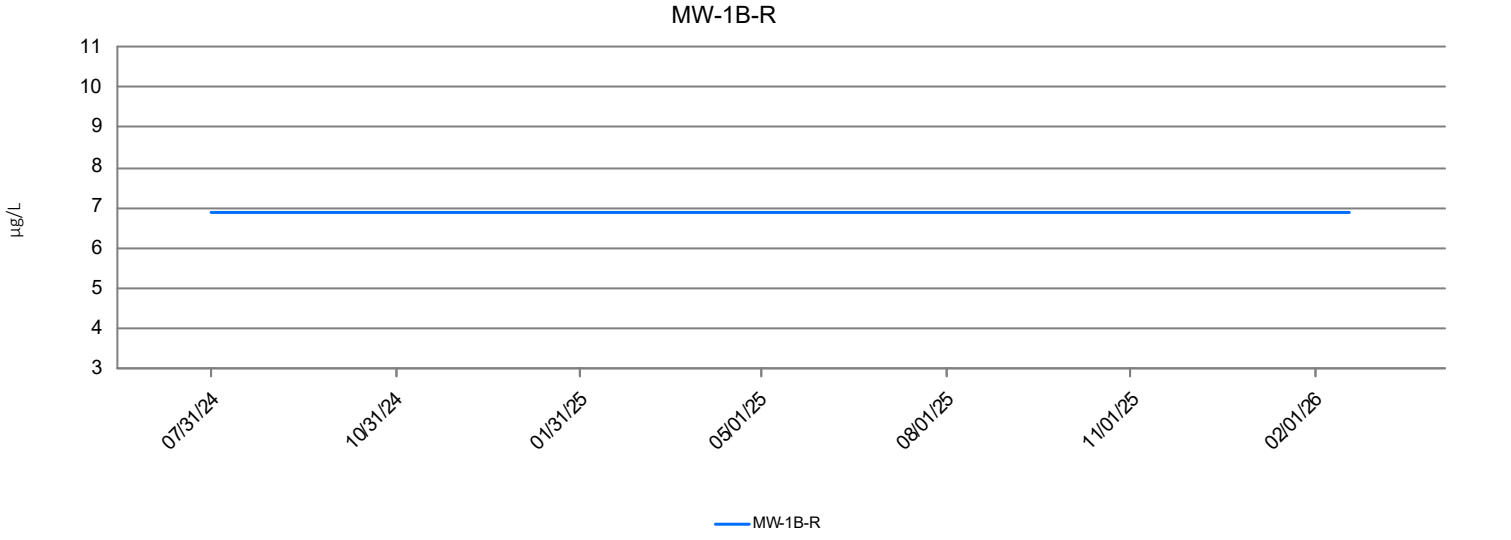
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Zinc, Total Recoverable (µg/L)







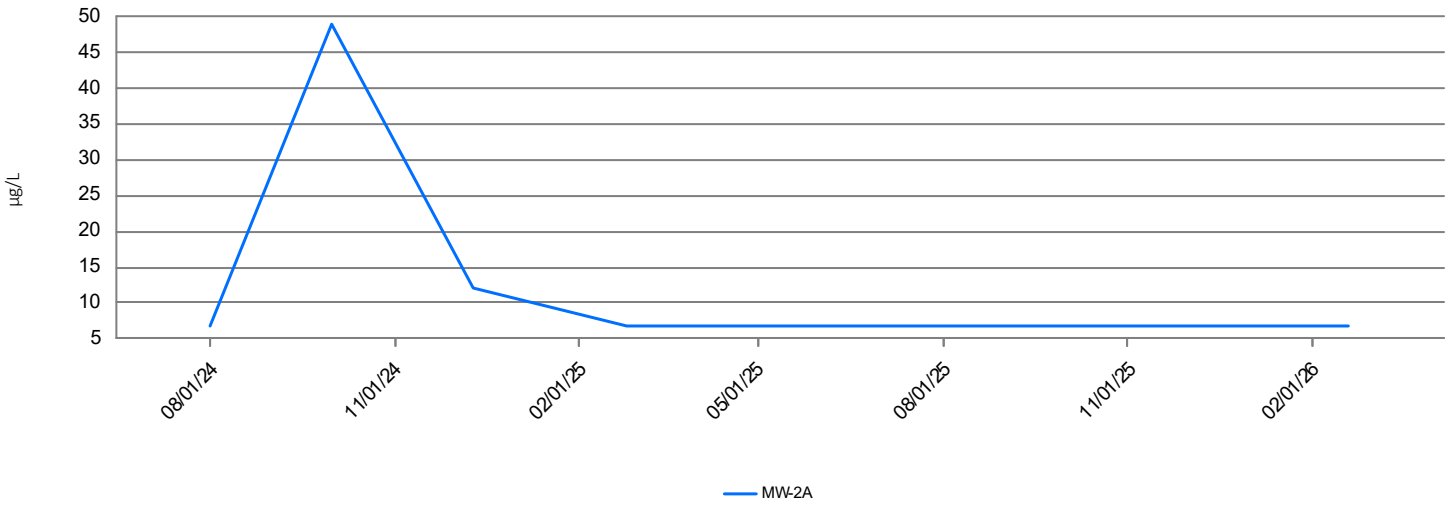
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

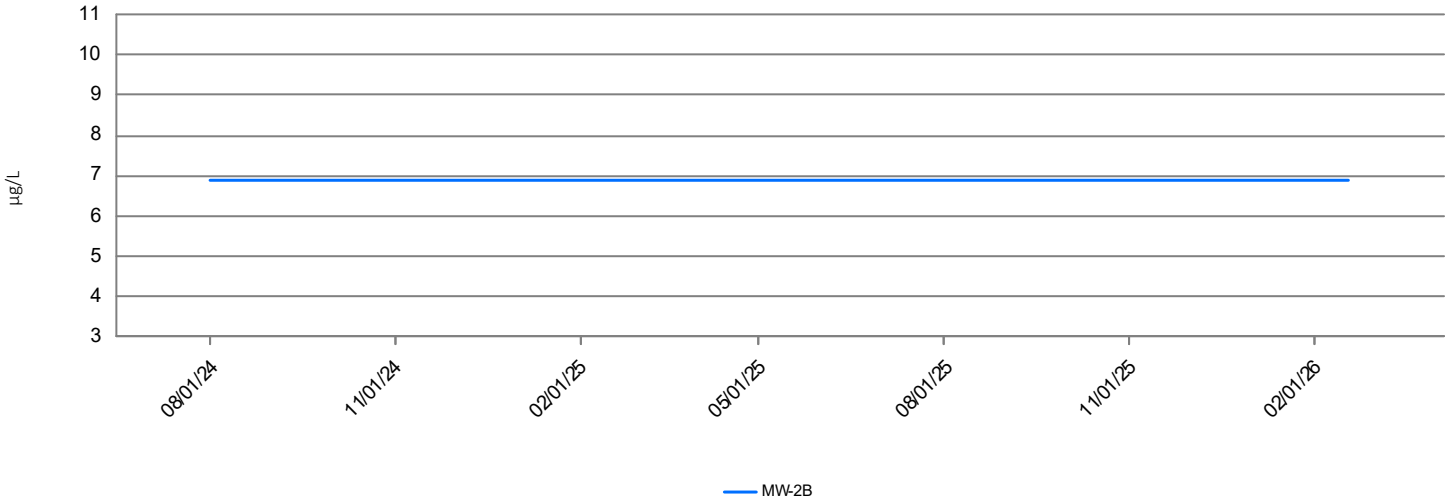
MonitorPro

No Group Selected, Zinc, Total Recoverable (µg/L)

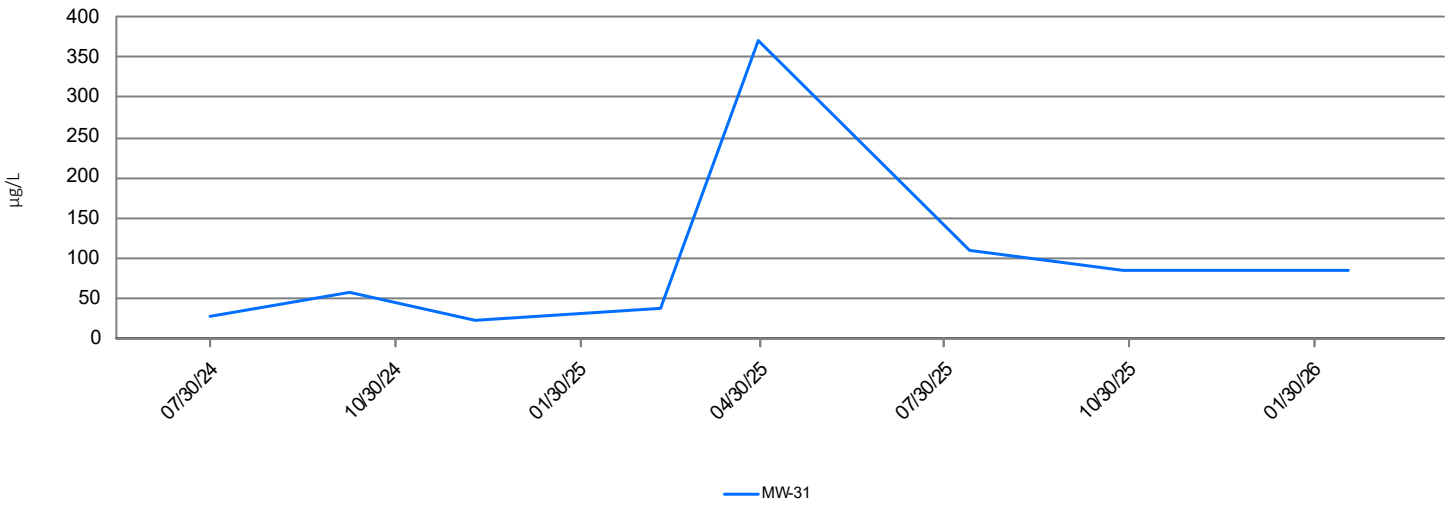
MW-2A



MW-2B



MW-31



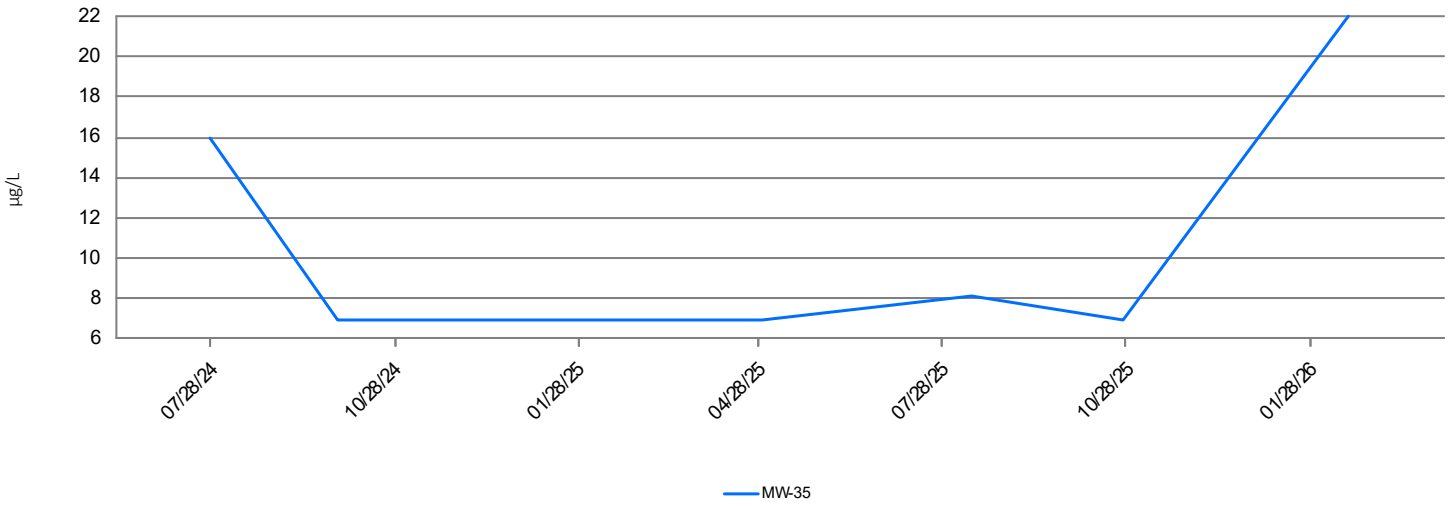
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

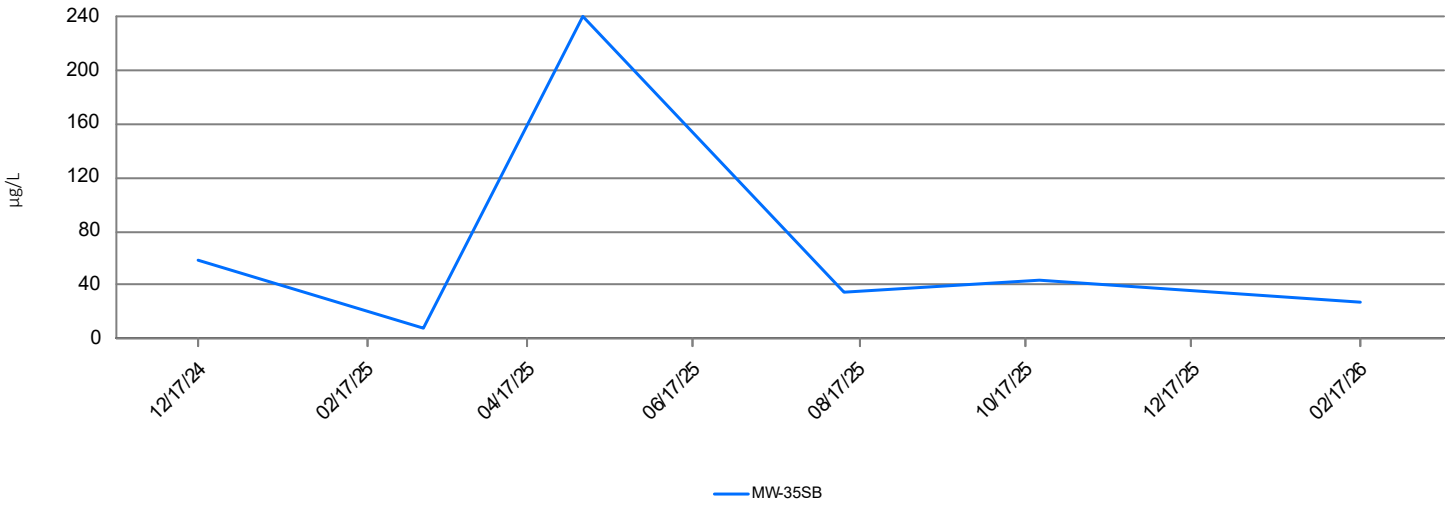
MonitorPro

No Group Selected, Zinc, Total Recoverable (µg/L)

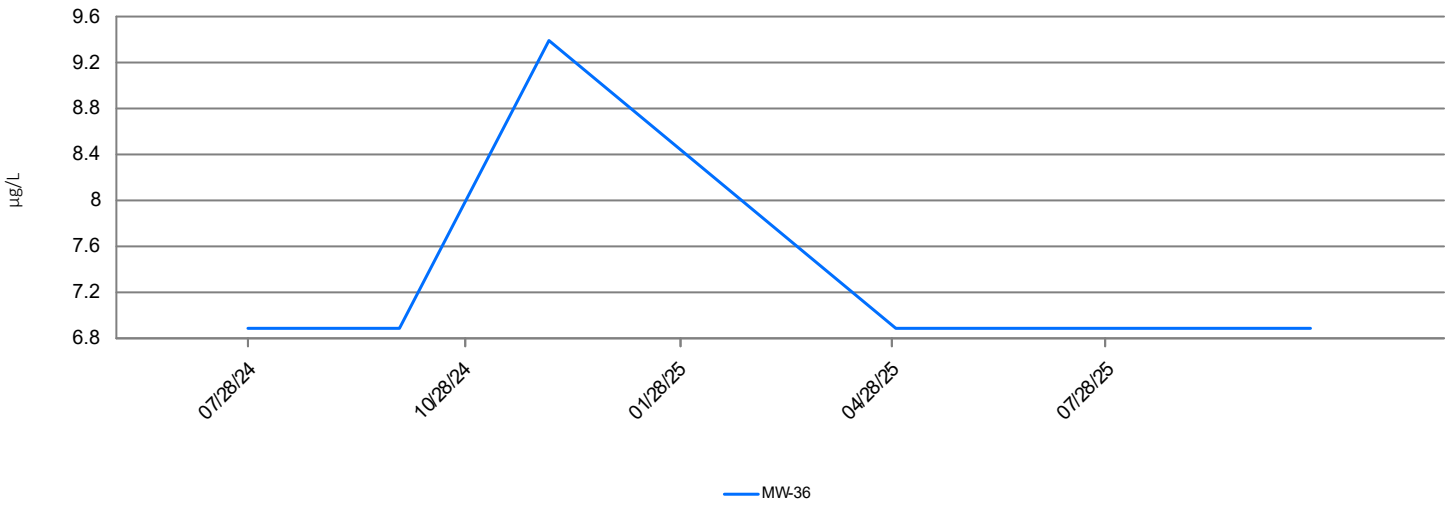
MW-35



MW-35SB



MW-36

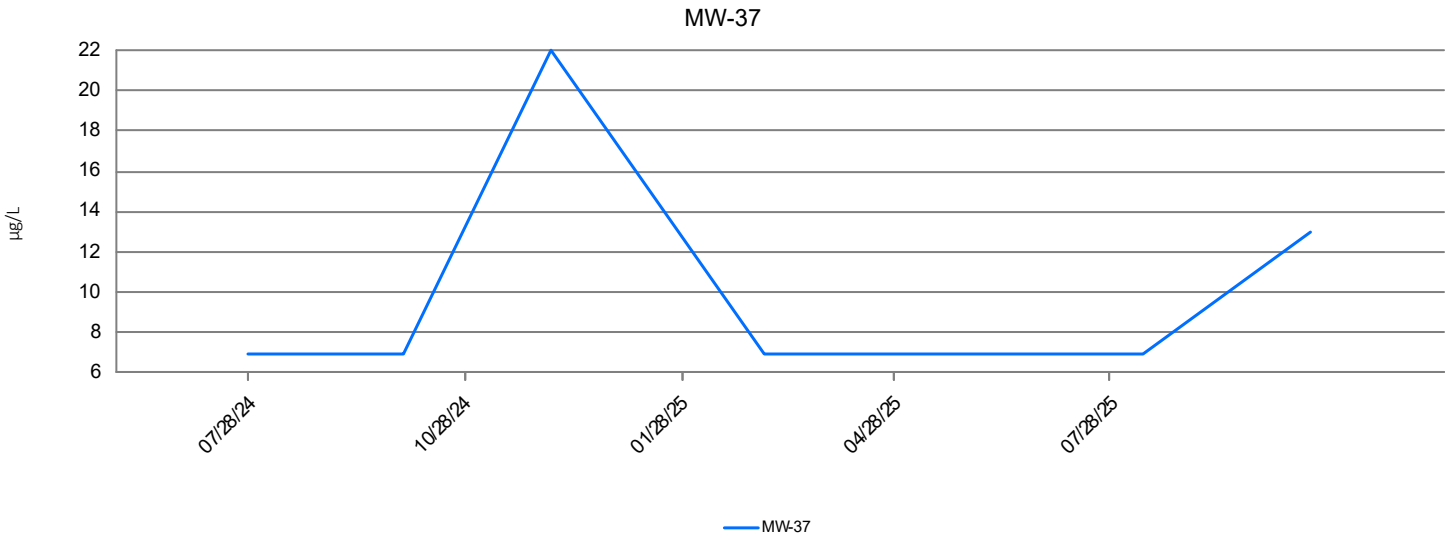


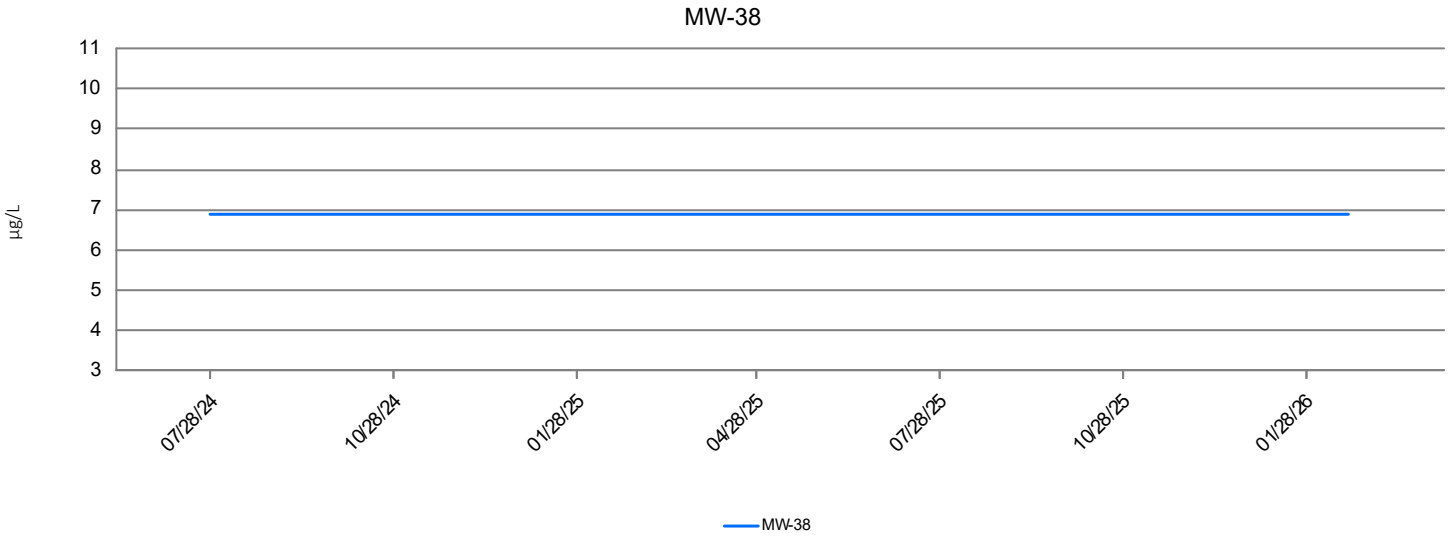
Variable Graphical Report

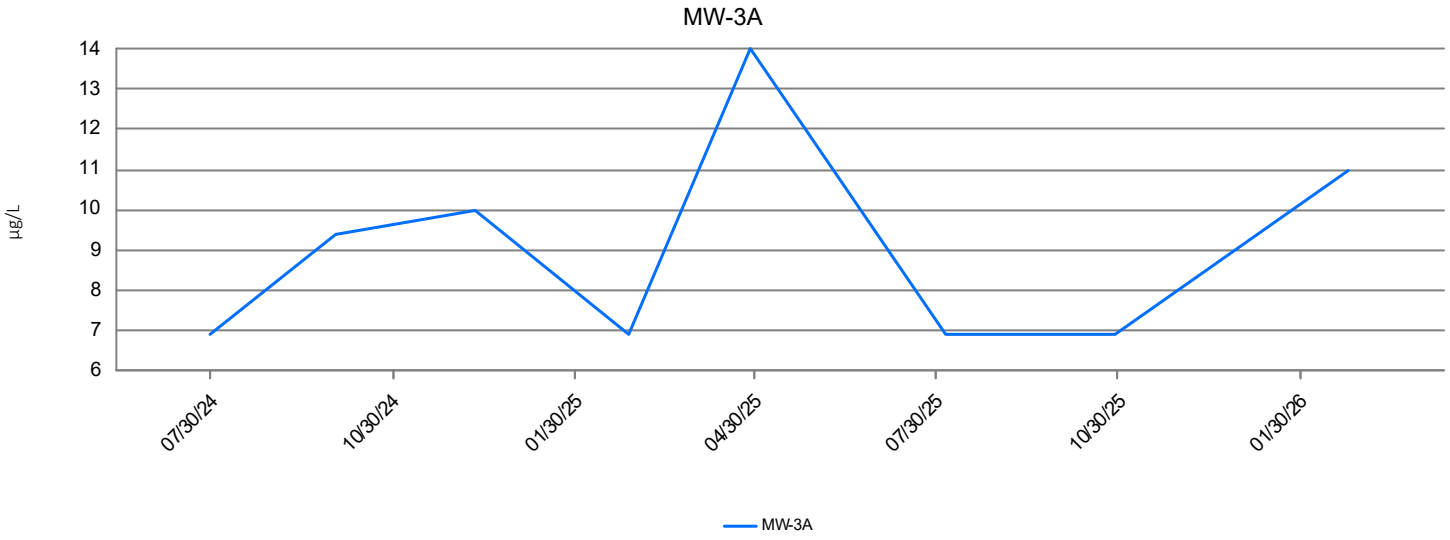
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Zinc, Total Recoverable (µg/L)







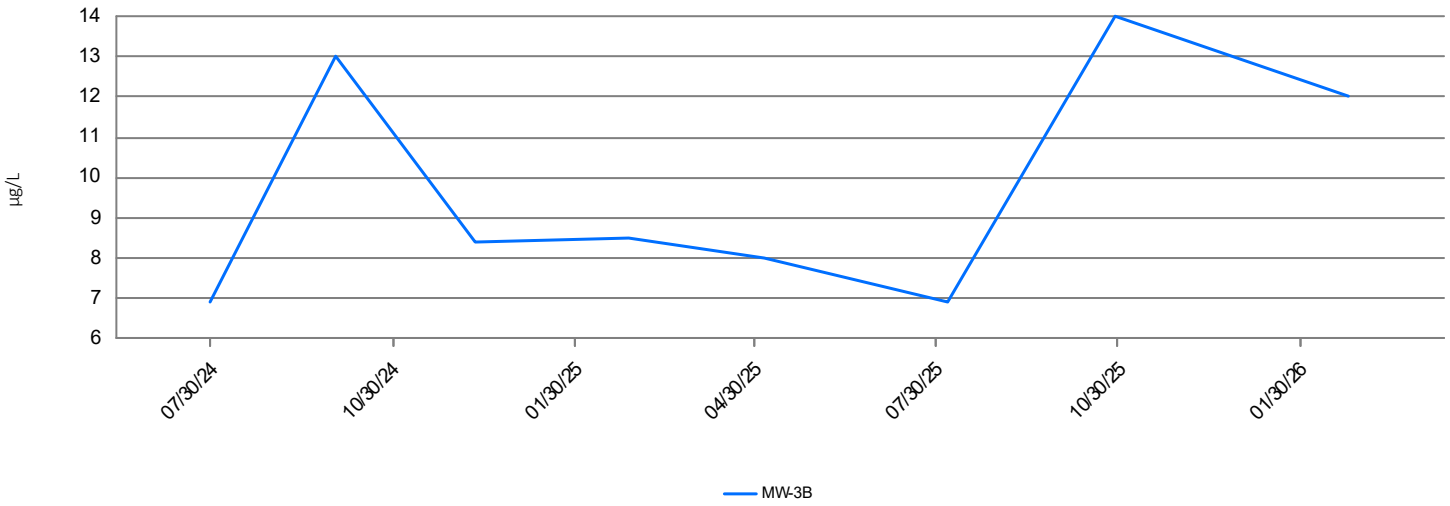
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

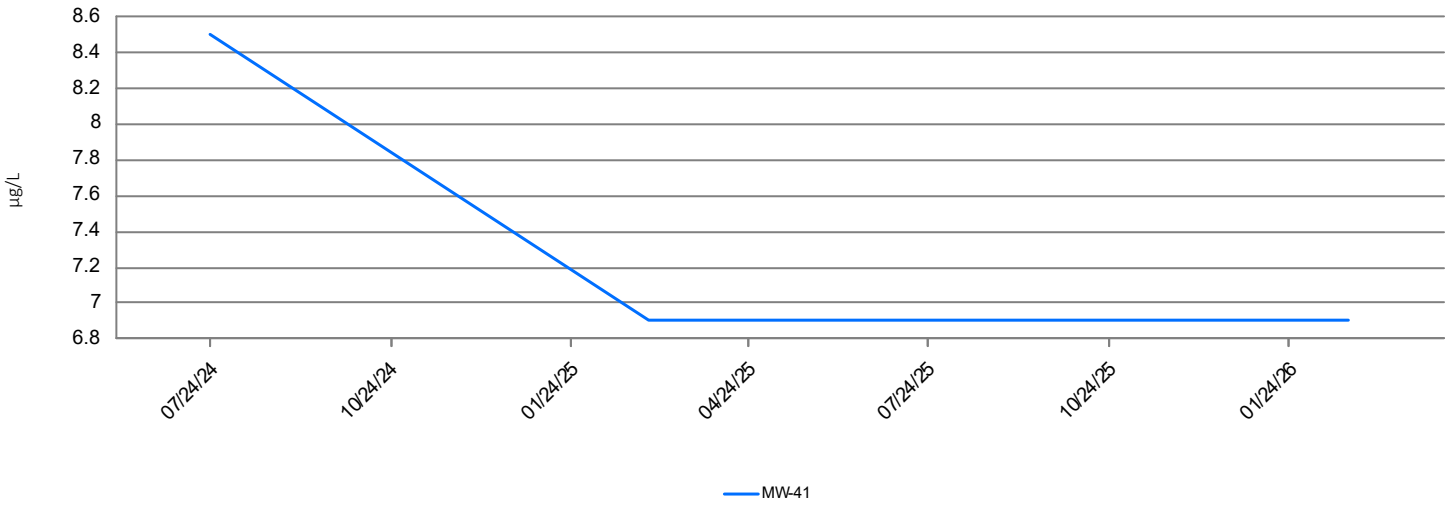
MonitorPro

No Group Selected, Zinc, Total Recoverable (µg/L)

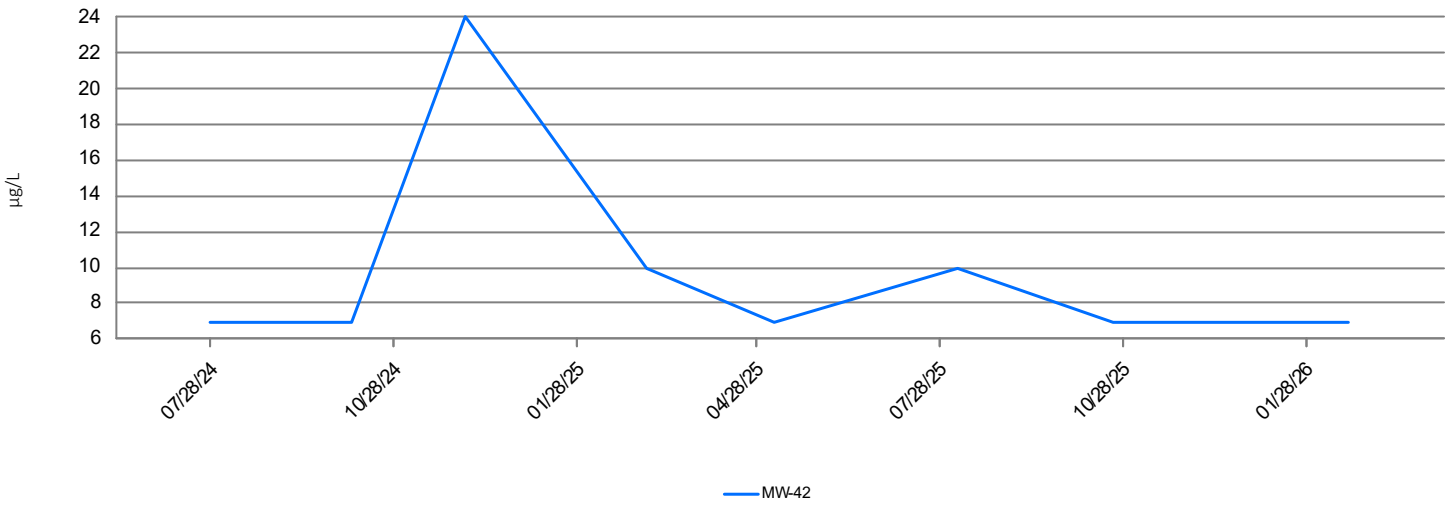
MW-3B



MW-41



MW-42



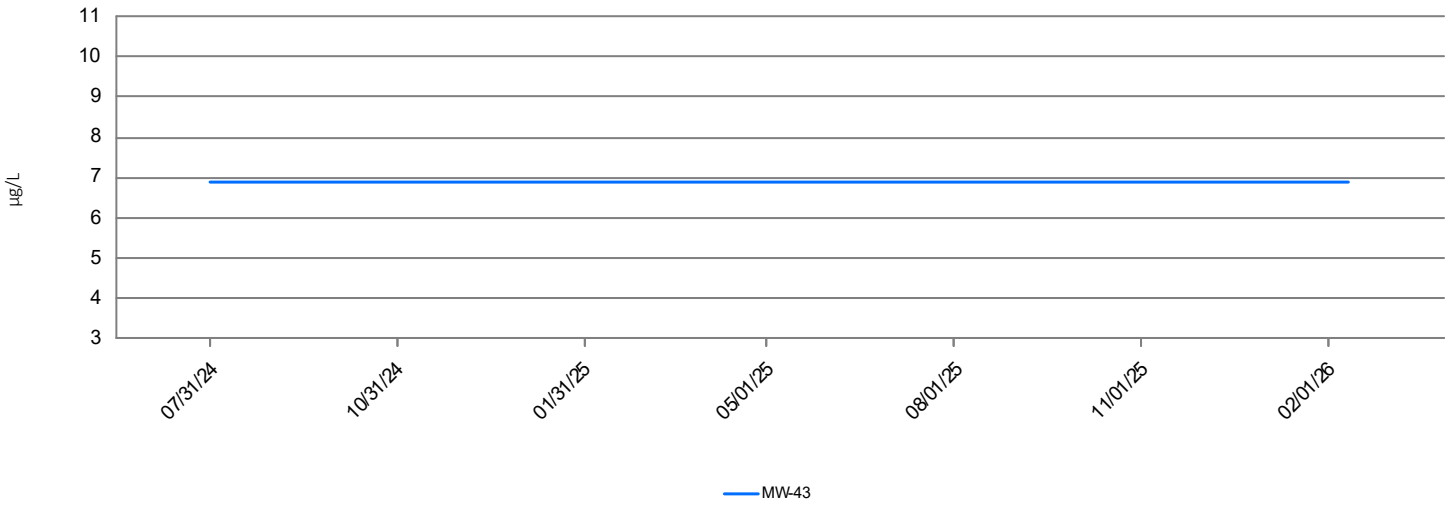
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

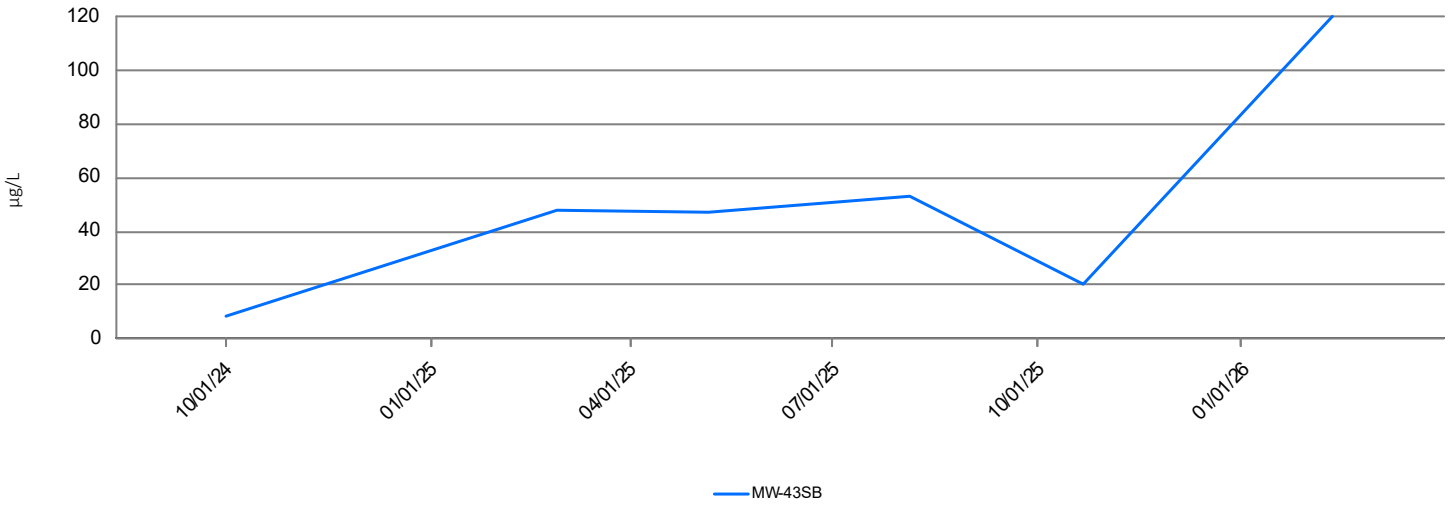
MonitorPro

No Group Selected, Zinc, Total Recoverable (µg/L)

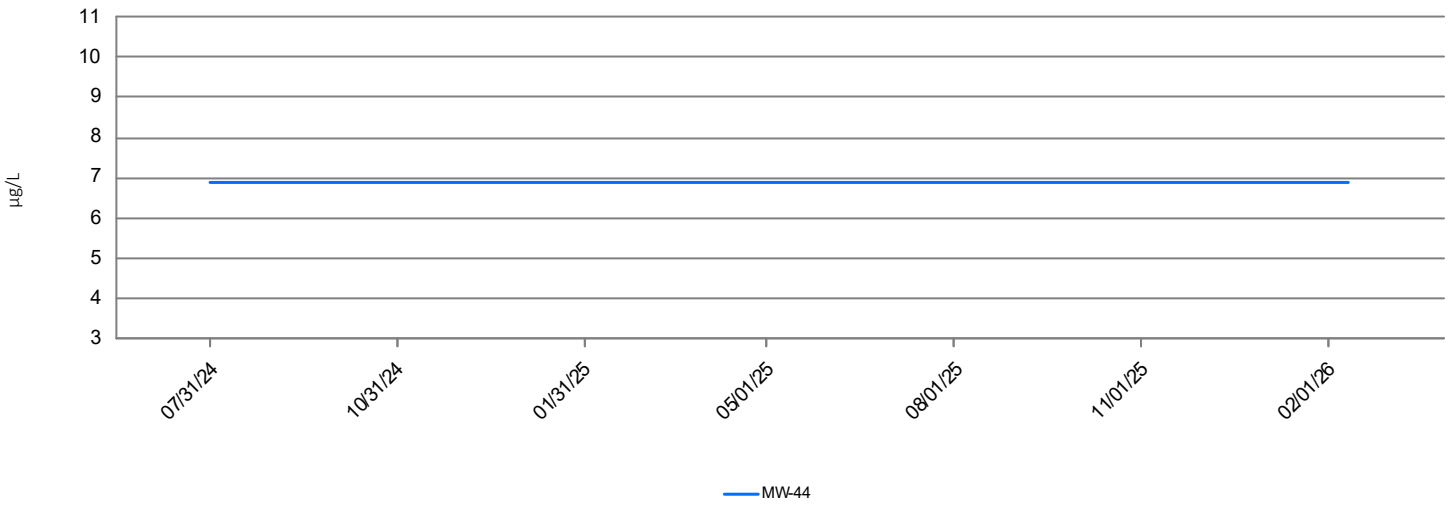
MW-43



MW-43SB



MW-44



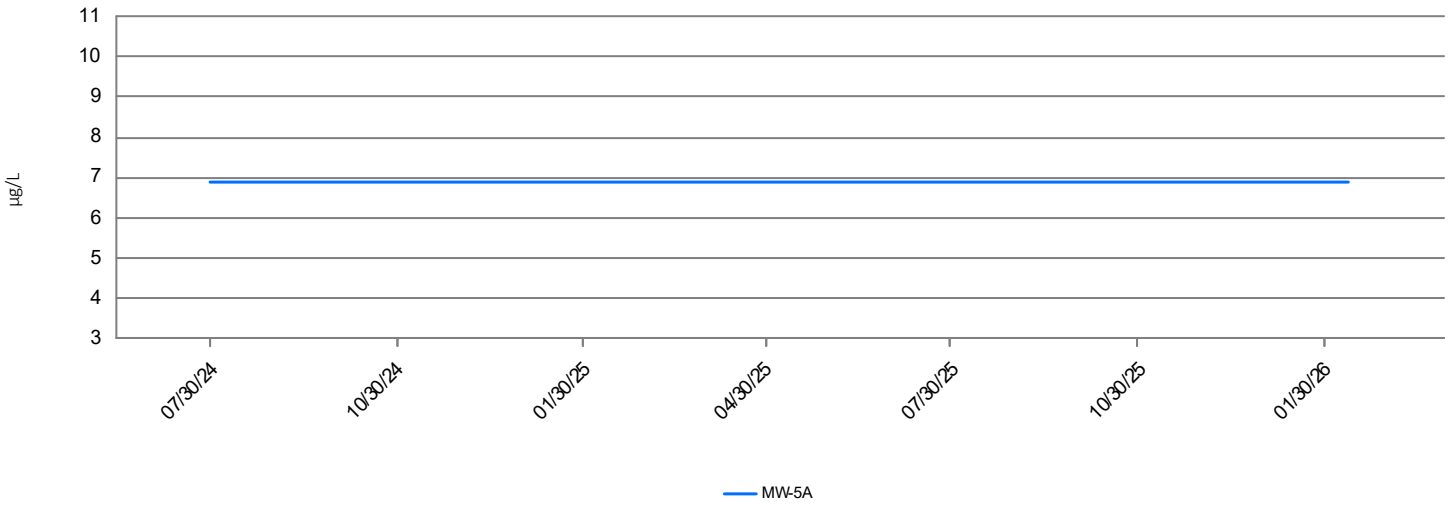
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

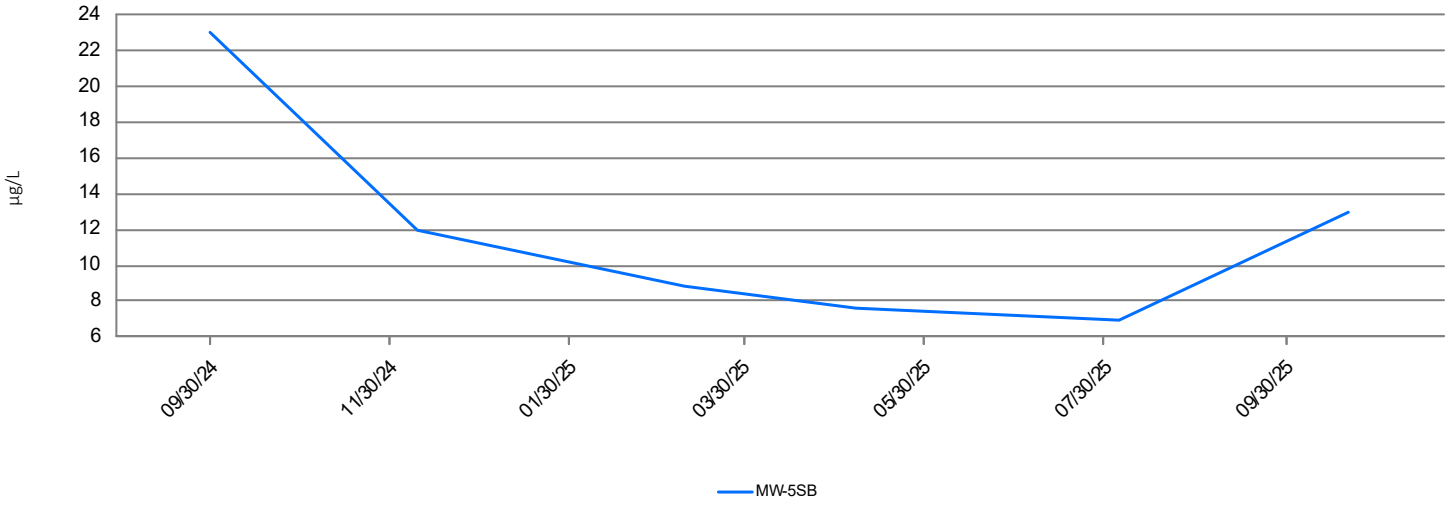
MonitorPro

No Group Selected, Zinc, Total Recoverable (µg/L)

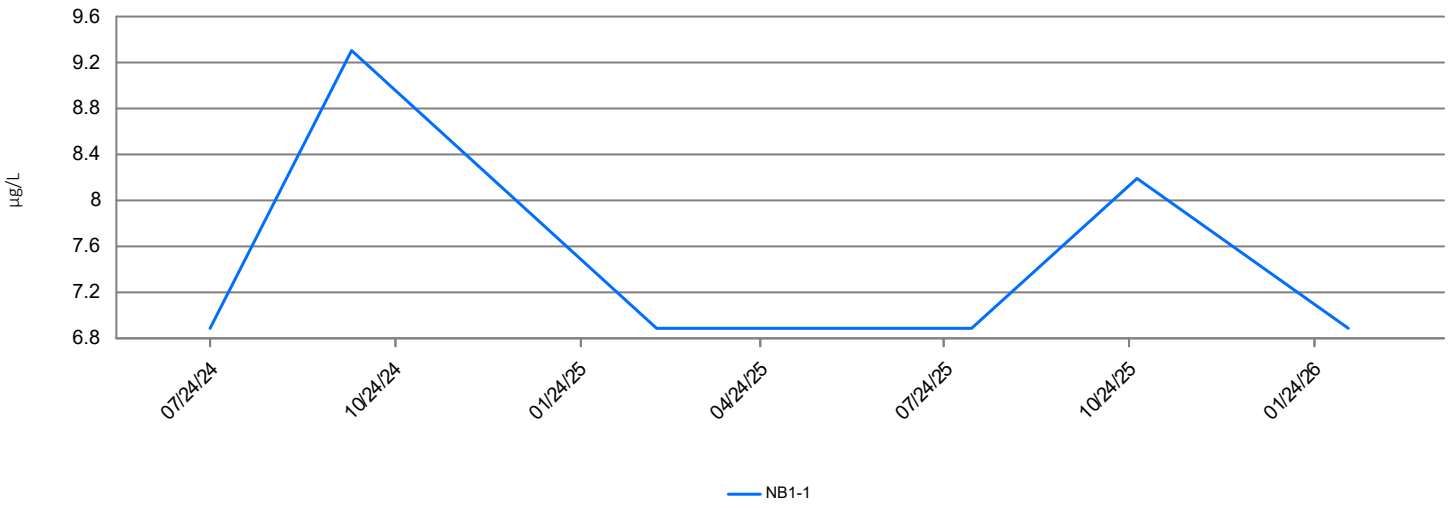
MW-5A



MW-5SB



NB1-1

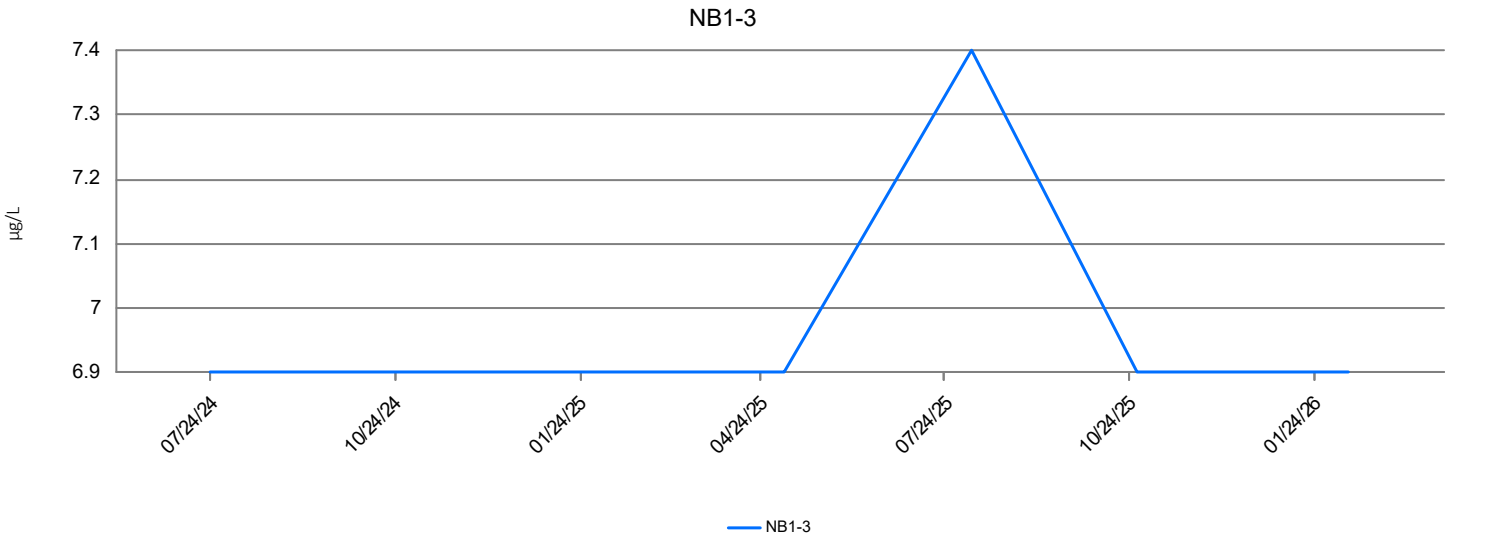


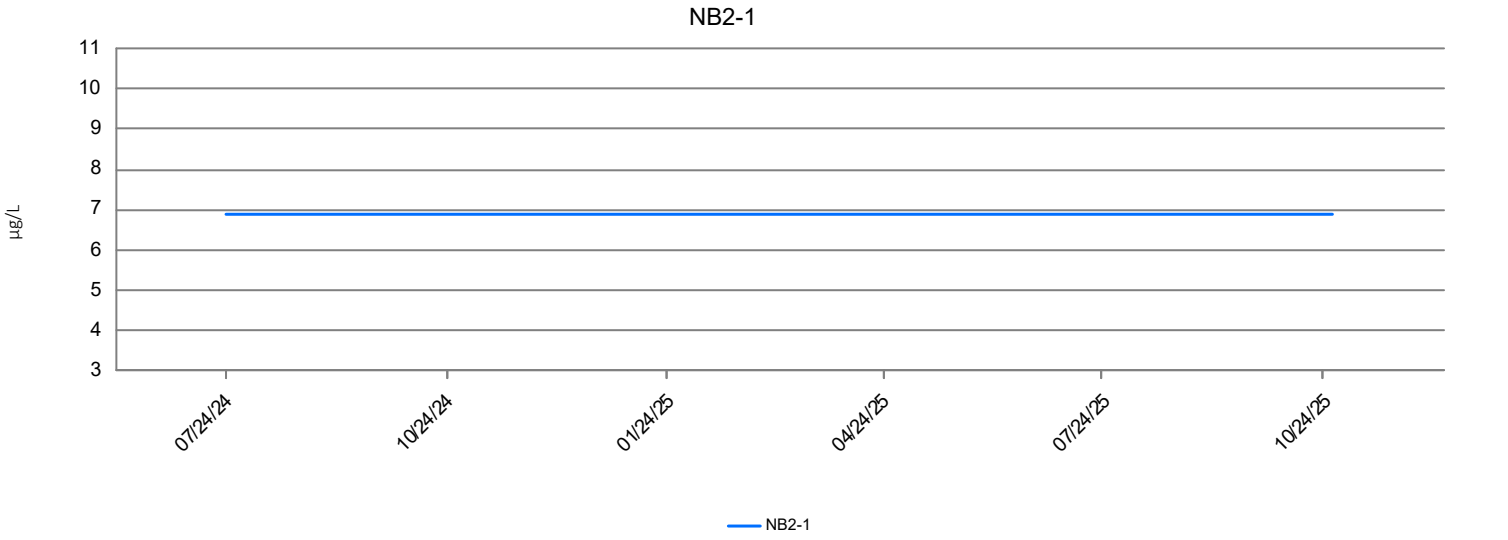
Variable Graphical Report

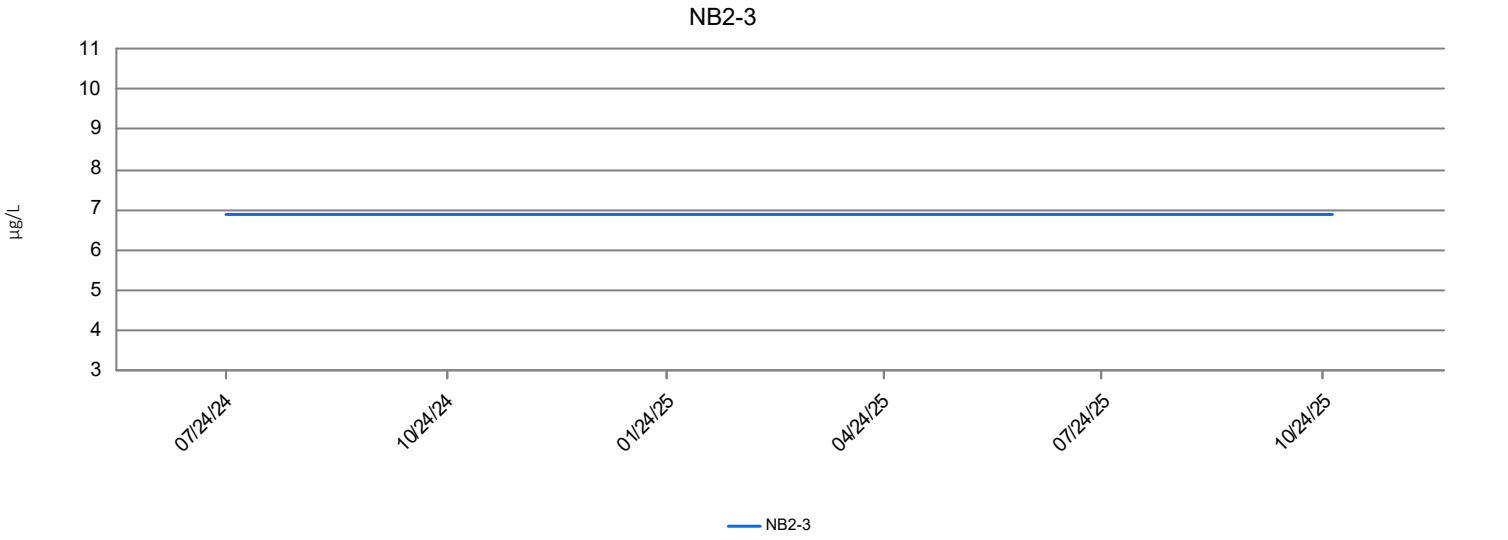
Date from 07/01/2024 to 05/01/2026

MonitorPro

No Group Selected, Zinc, Total Recoverable (µg/L)







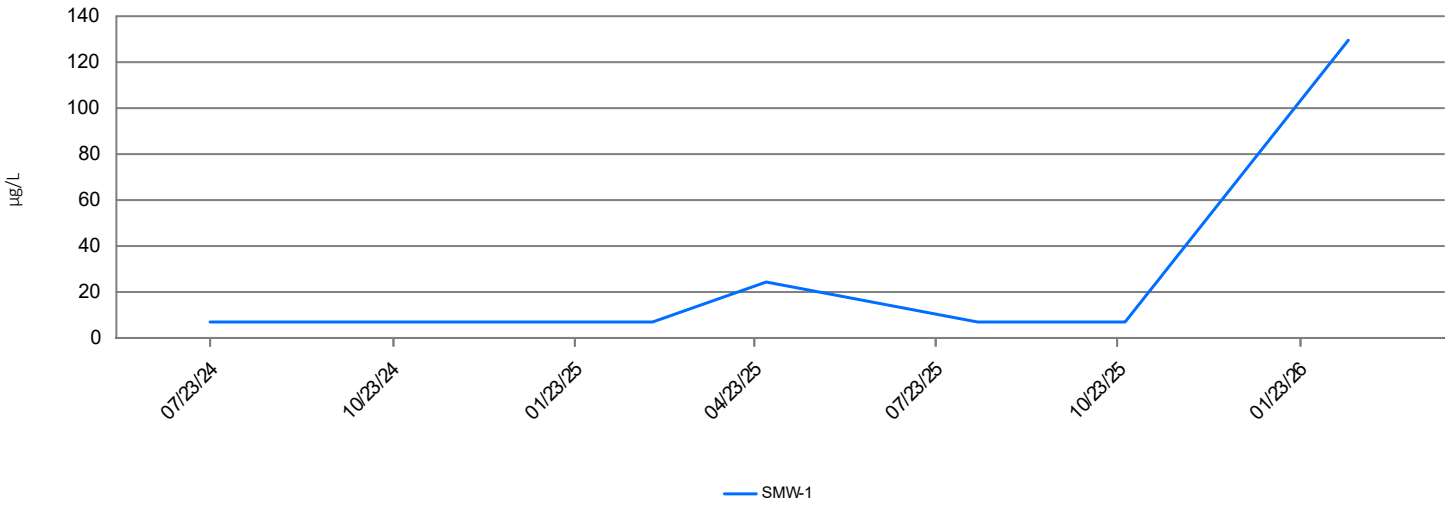
Variable Graphical Report

Date from 07/01/2024 to 05/01/2026

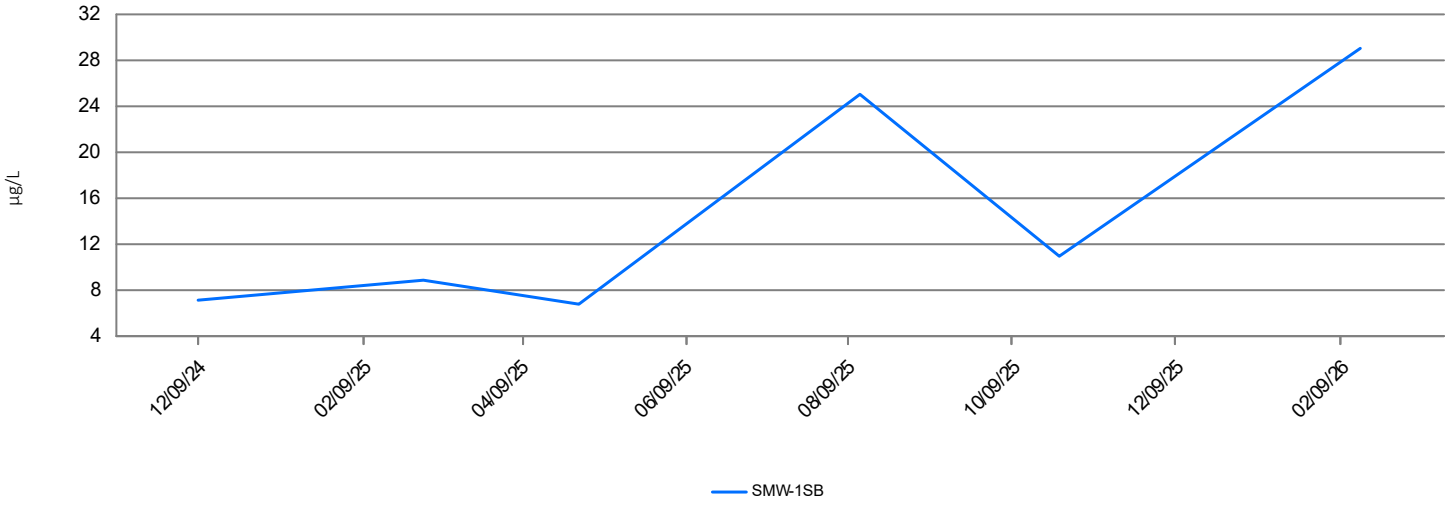
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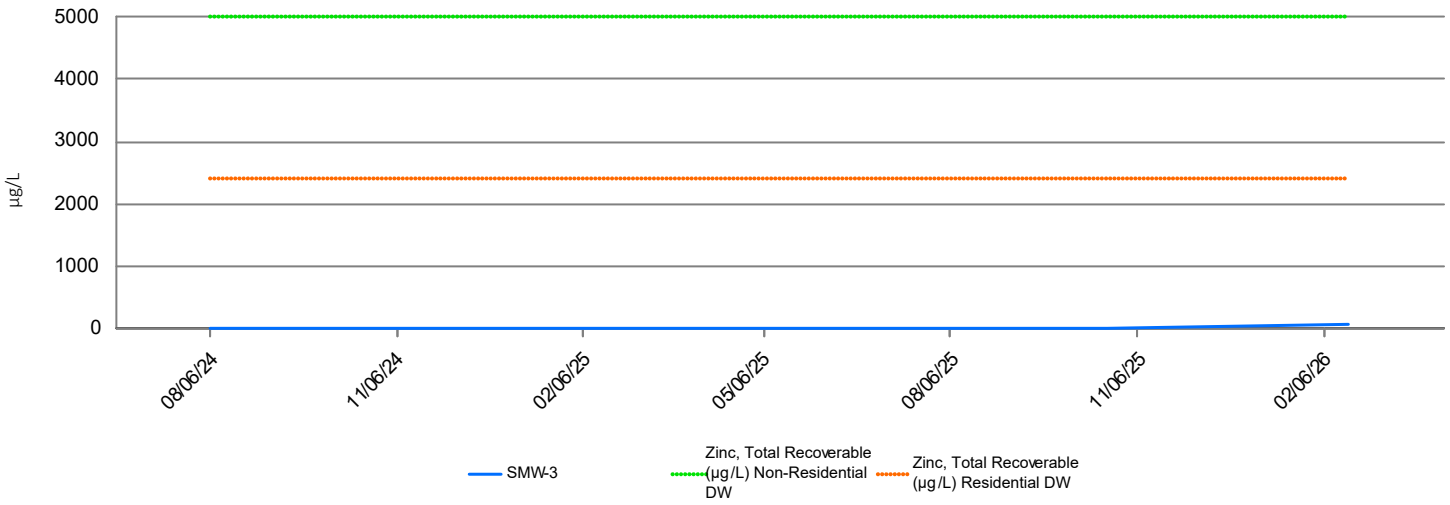
SMW-1



SMW-1SB



SMW-3

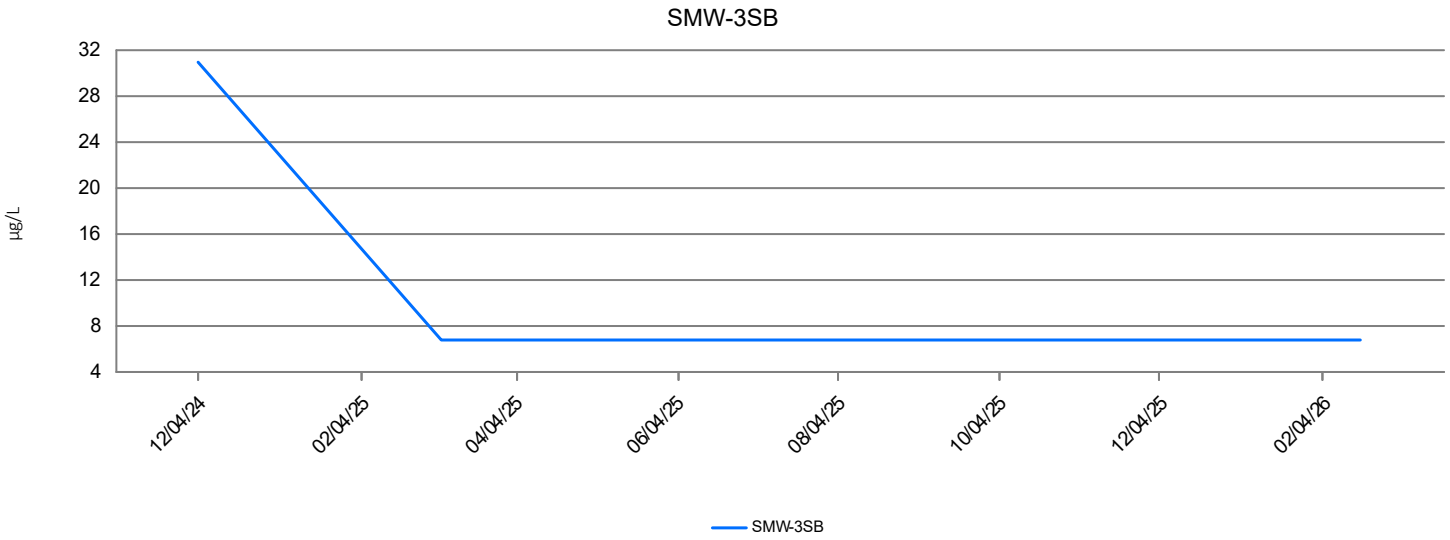


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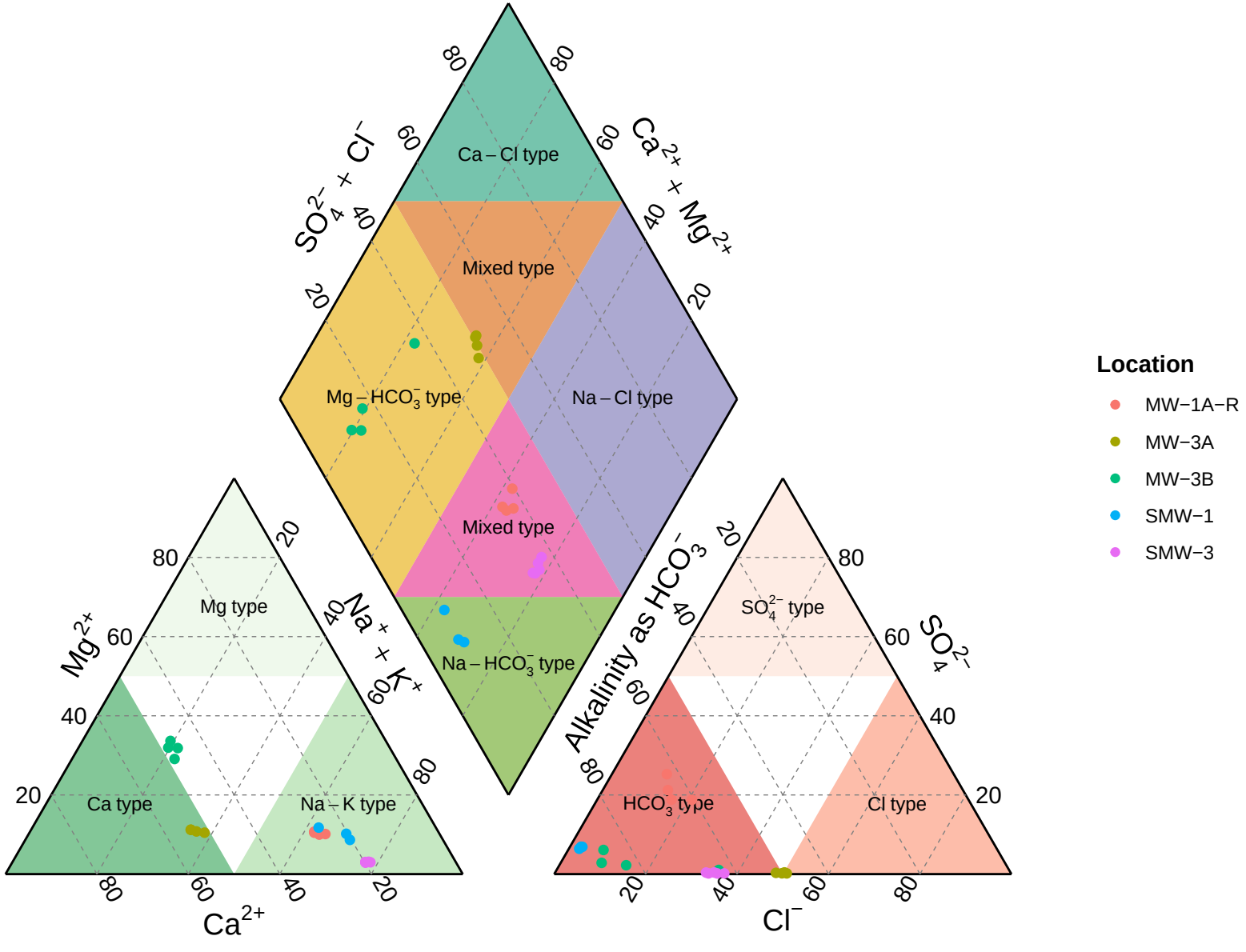
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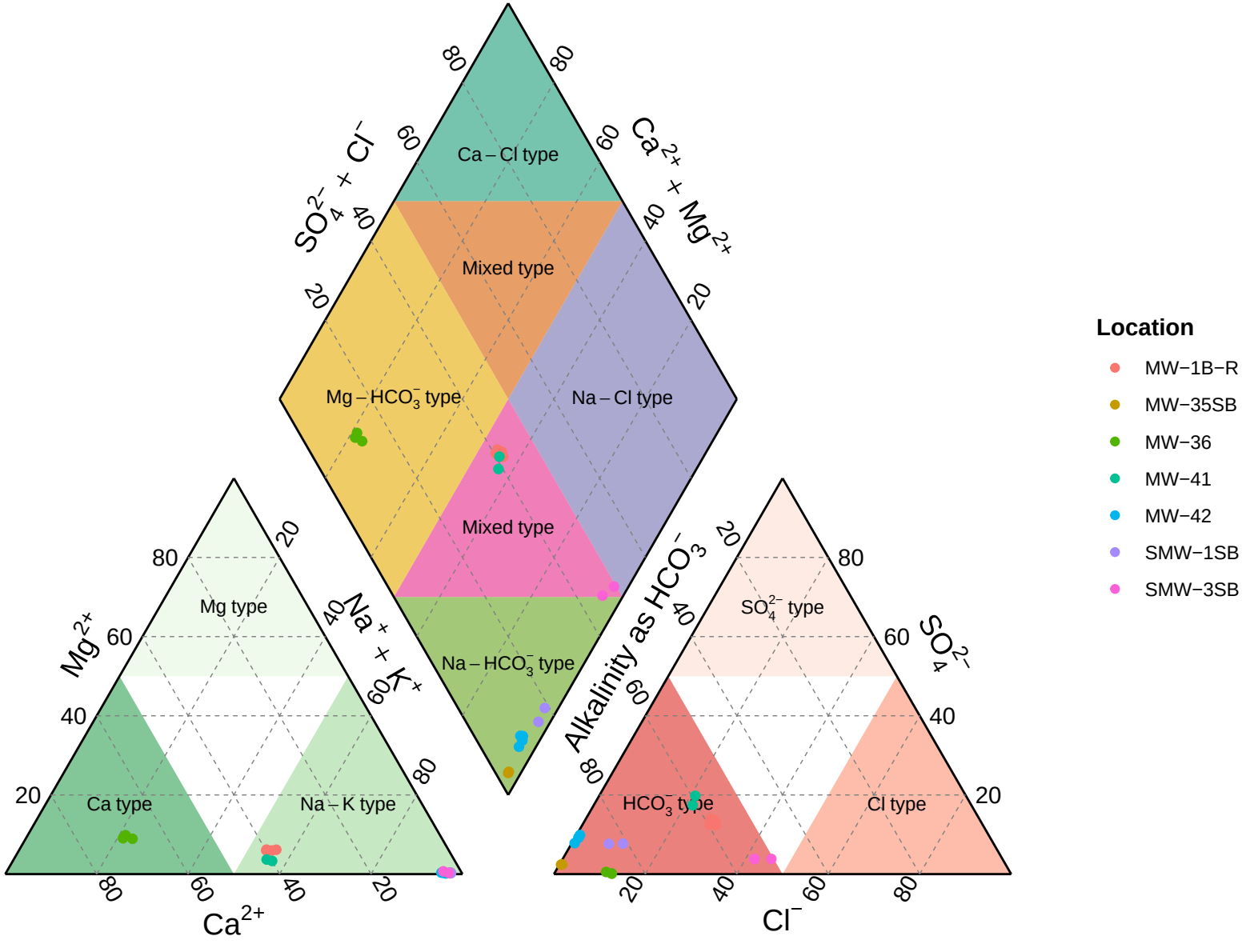


H-2
Trilinear Diagrams

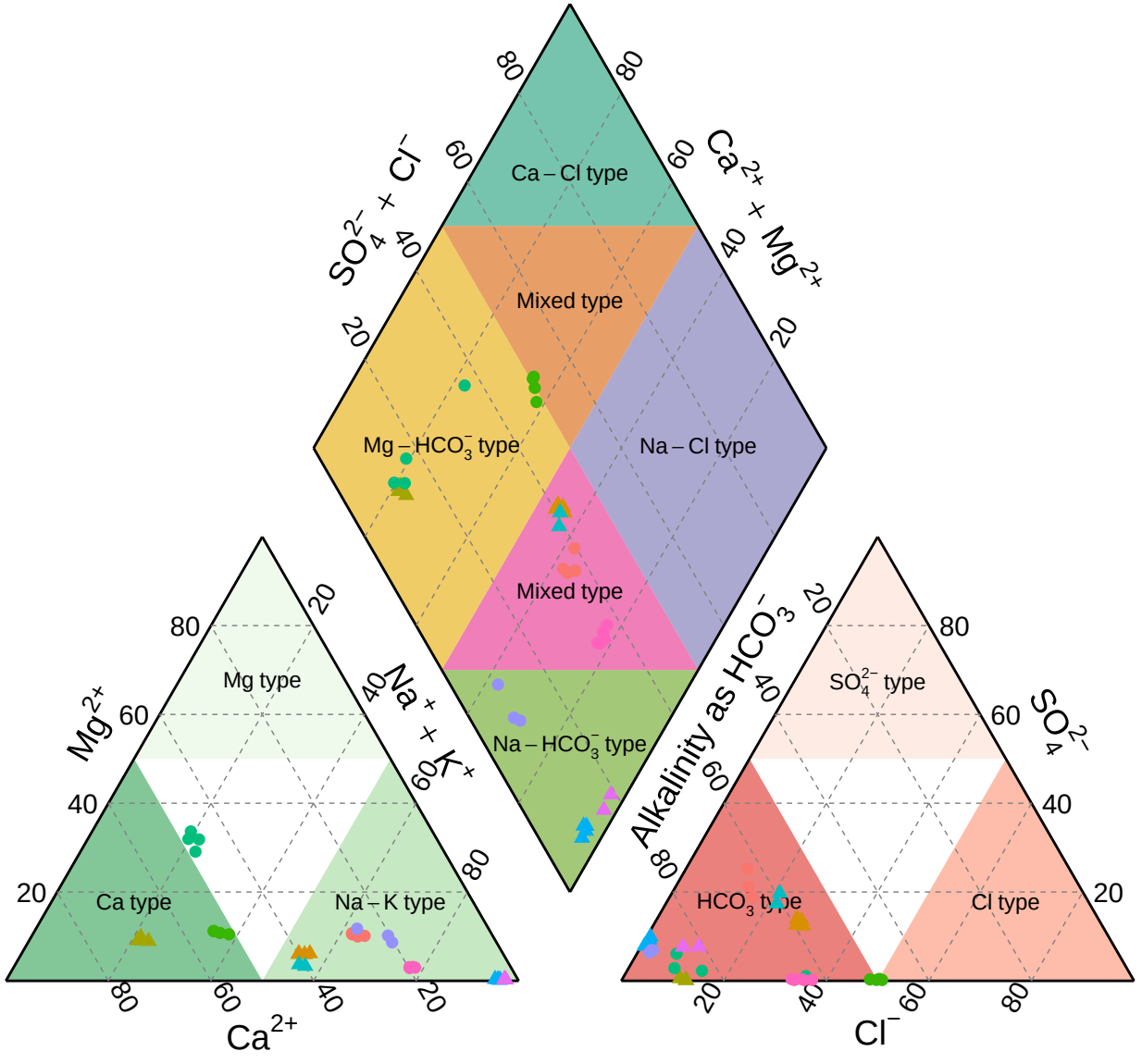
Trilinear Plot of Groundwater Major Ion Chemistry: Unconsolidated Deposits Wells



Trilinear Plot of Groundwater Major Ion Chemistry: Shallow Bedrock Wells



Trilinear Plot of Groundwater Major Ion Chemistry:
Wells With Screen Mid−Point Depth(ft): 0 to 100



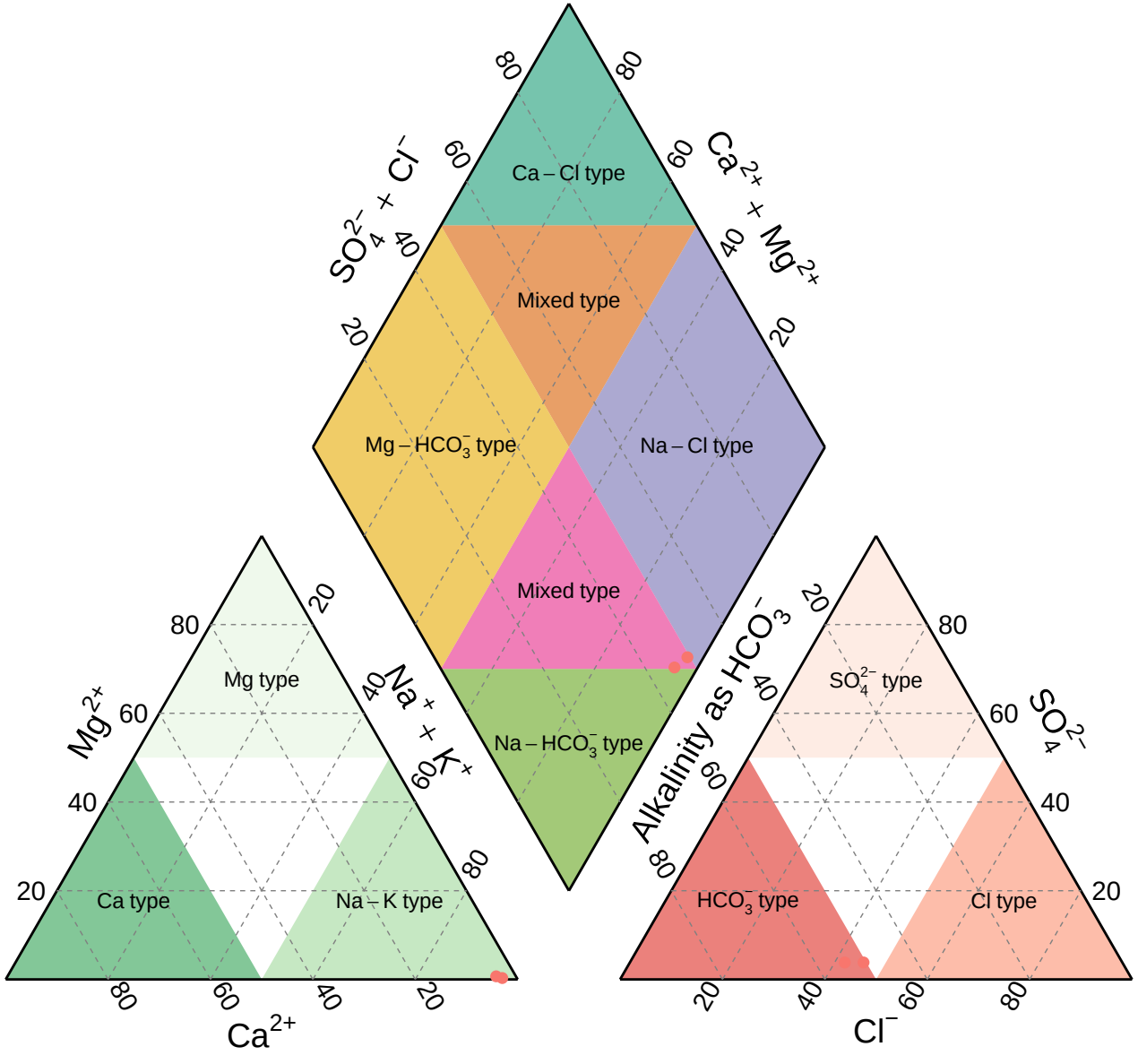
Location

- MW−1A−R
- MW−1B−R
- MW−36
- MW−3A
- MW−3B
- MW−41
- MW−42
- SMW−1
- SMW−1SB
- SMW−3

Screen Geology

- Overburden
- Shallow Bedrock

Trilinear Plot of Groundwater Major Ion Chemistry:
Wells With Screen Mid-Point Depth(ft): 100 to 200



Location

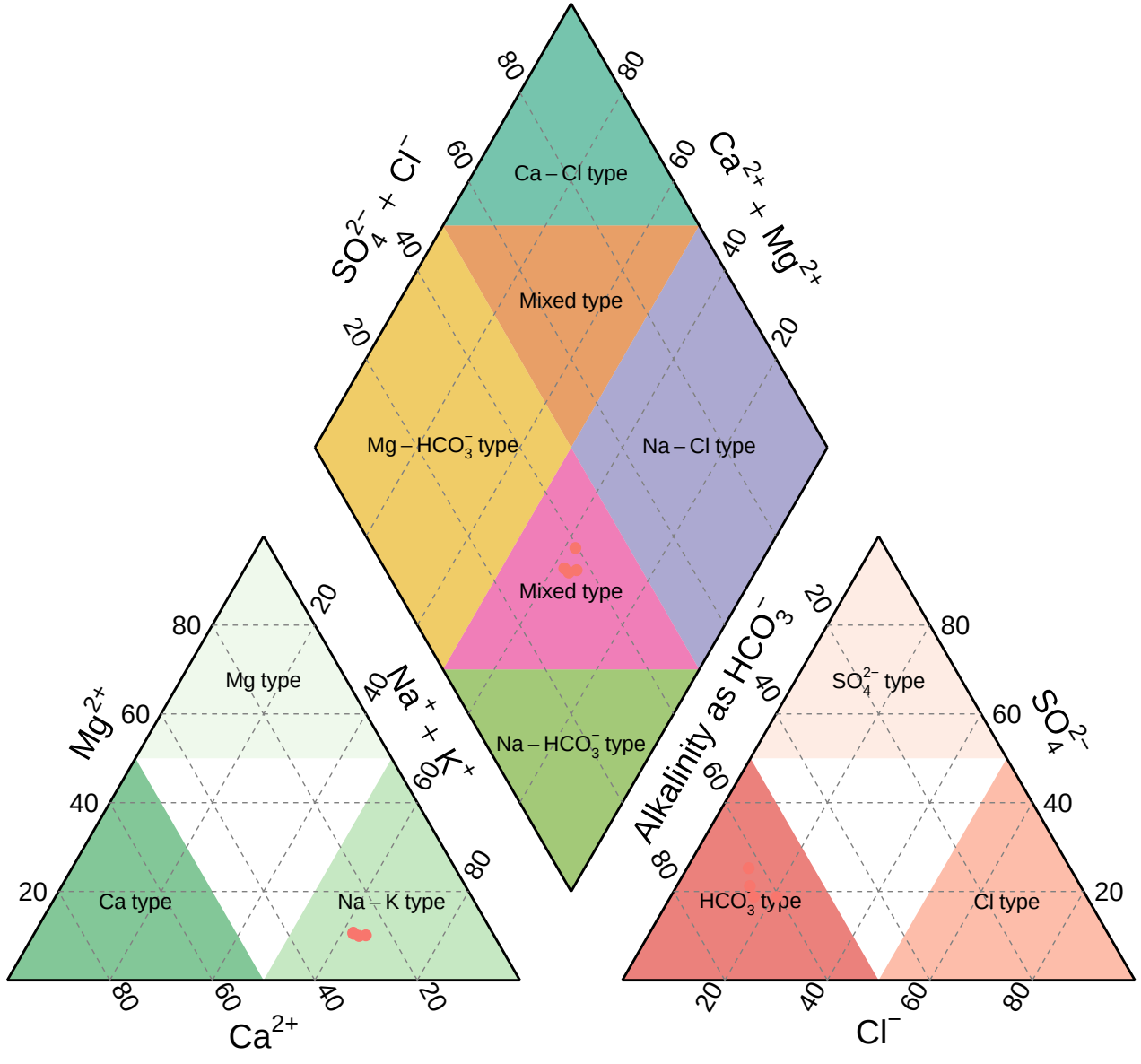
- SMW−3SB

Screen Geology

- Shallow Bedrock

Individual Monitoring Well Plots

Trilinear Plot of Groundwater Major Ion Chemistry: Well MW-1A-R



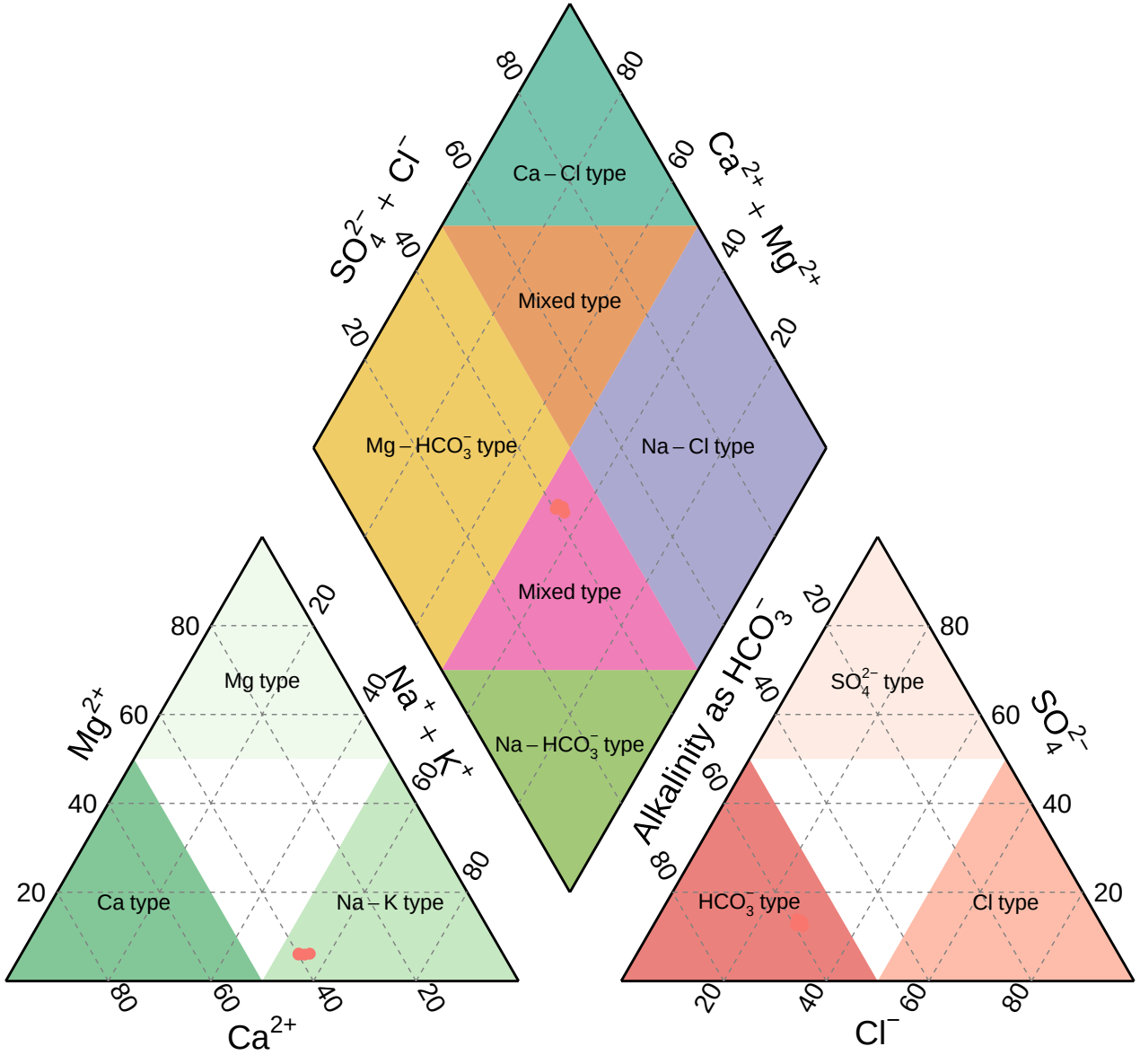
Location

- MW−1A−R

Screen Geology

- Overburden

Trilinear Plot of Groundwater Major Ion Chemistry: Well MW-1B-R



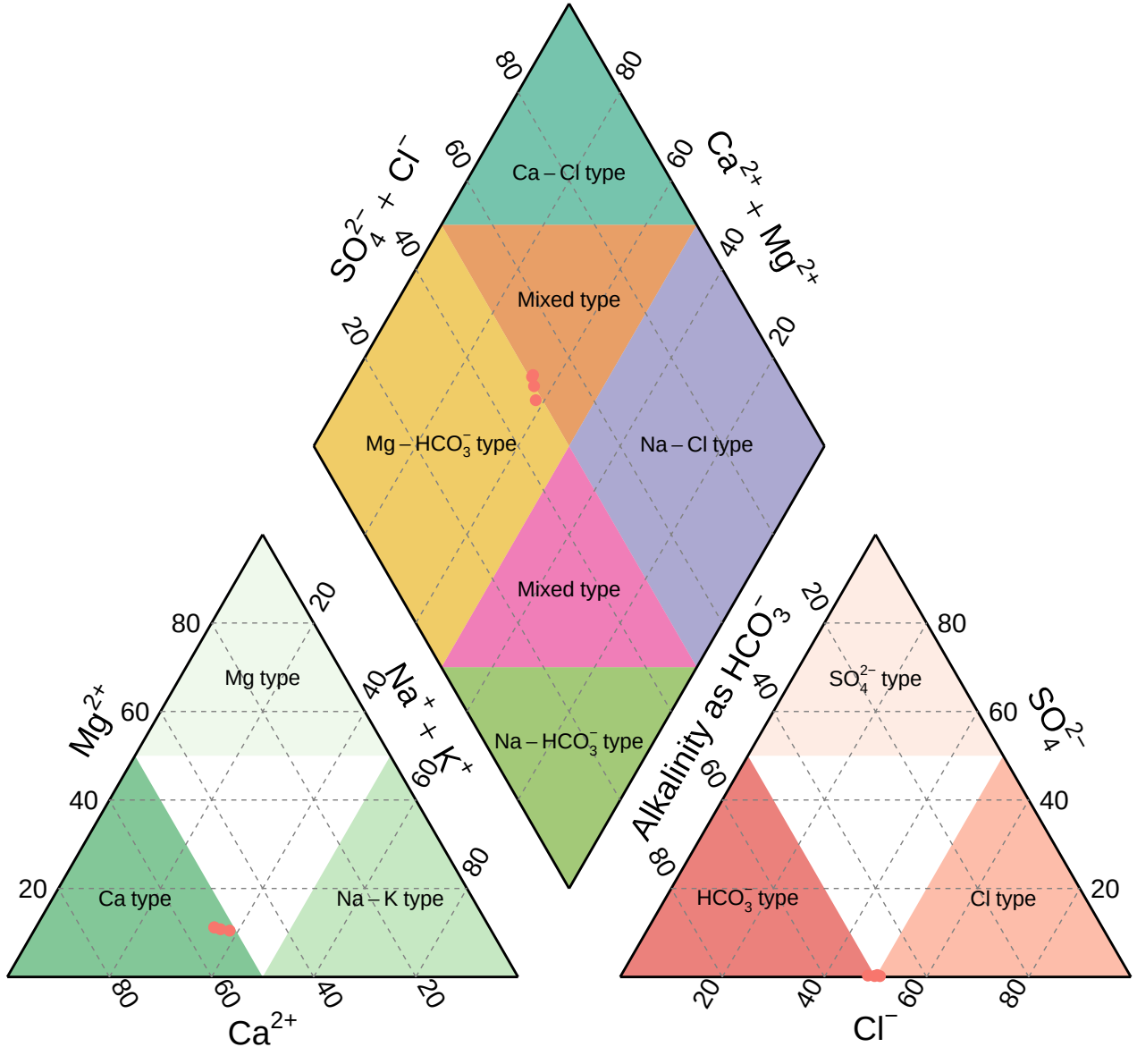
Location

- MW−1B−R

Screen Geology

- Shallow Bedrock

Trilinear Plot of Groundwater Major Ion Chemistry: Well MW-3A



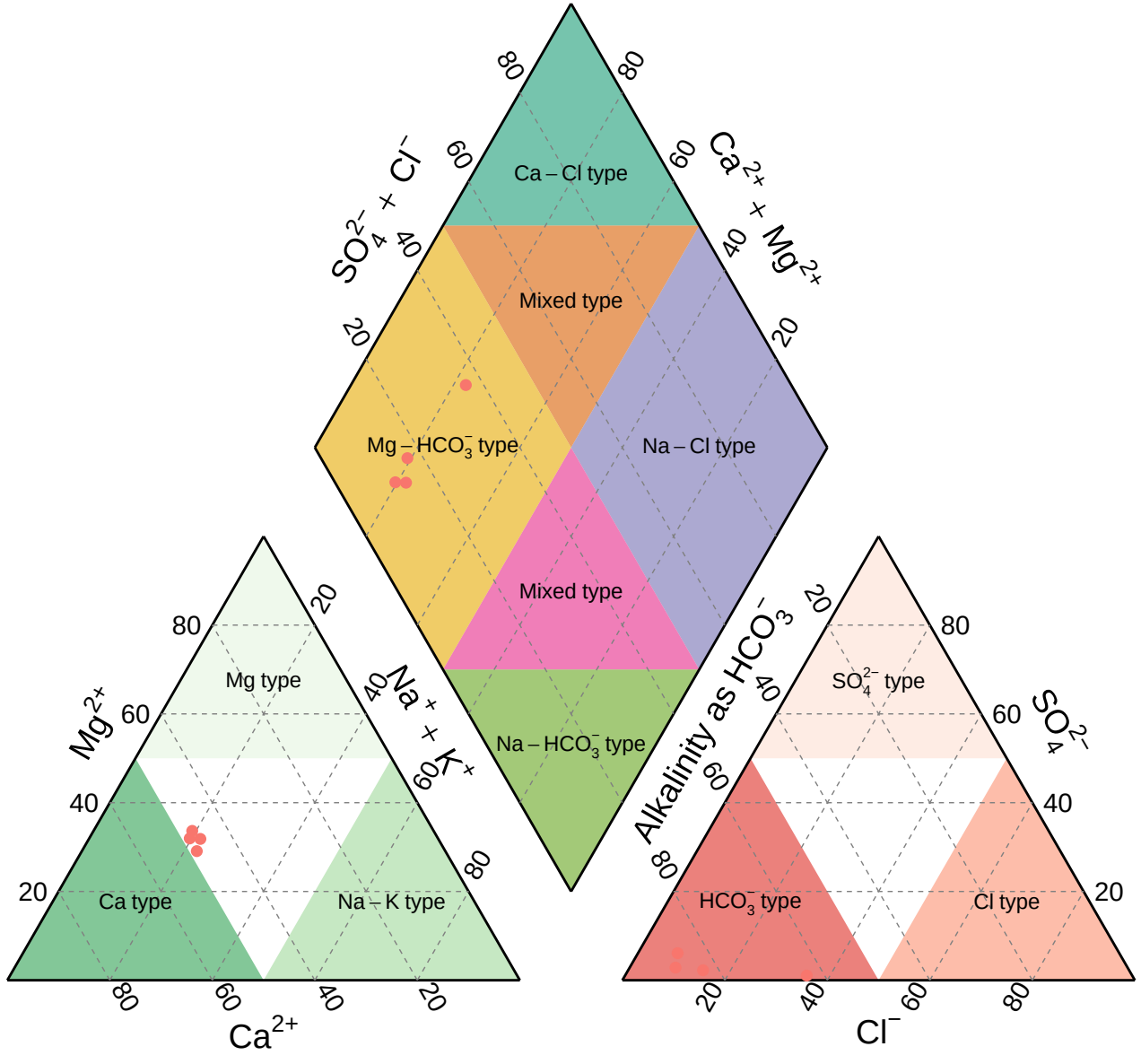
Location

- MW−3A

Screen Geology

- Overburden

Trilinear Plot of Groundwater Major Ion Chemistry: Well MW-3B



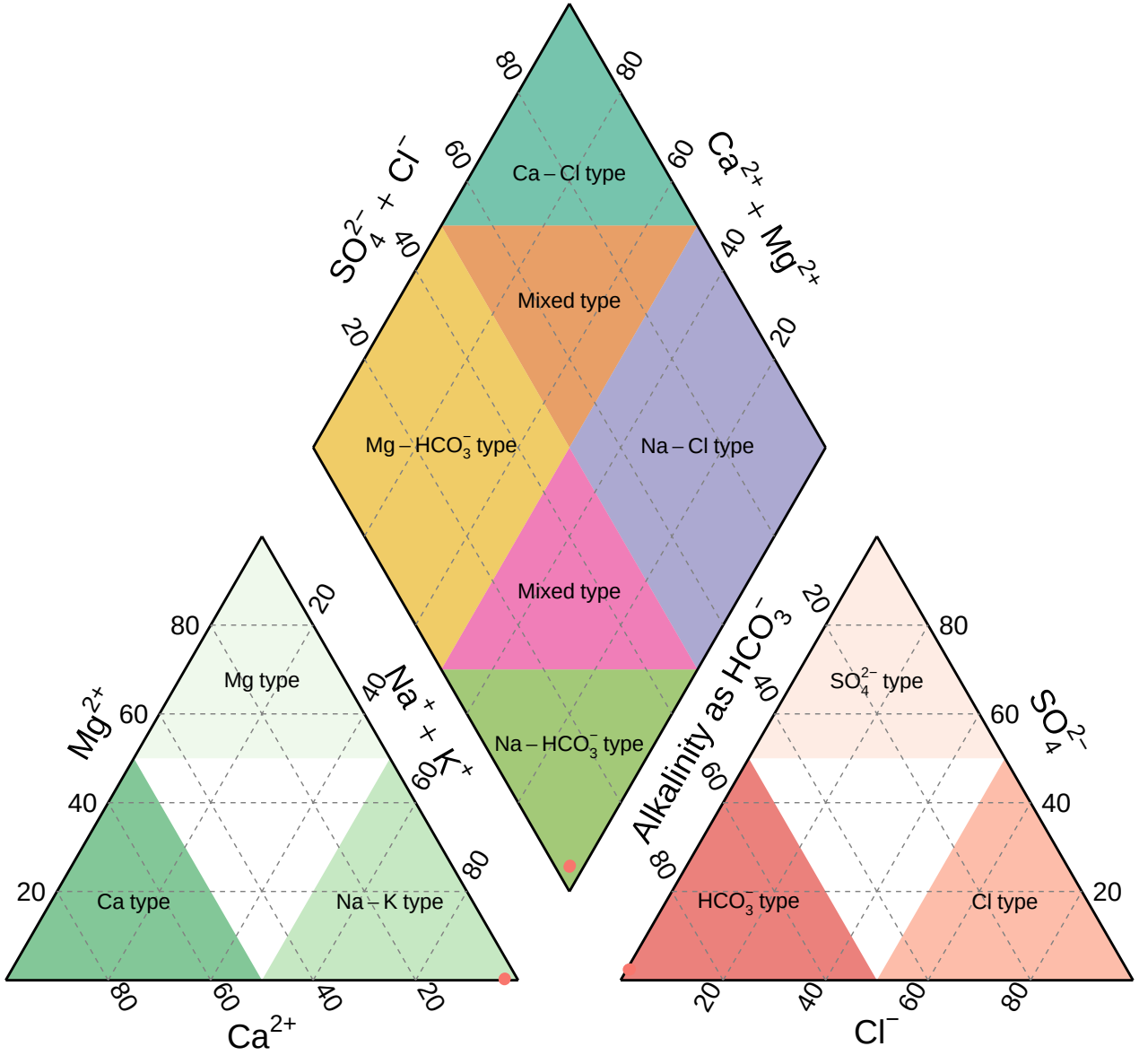
Location

- MW−3B

Screen Geology

- Overburden

Trilinear Plot of Groundwater Major Ion Chemistry: Well MW-35SB



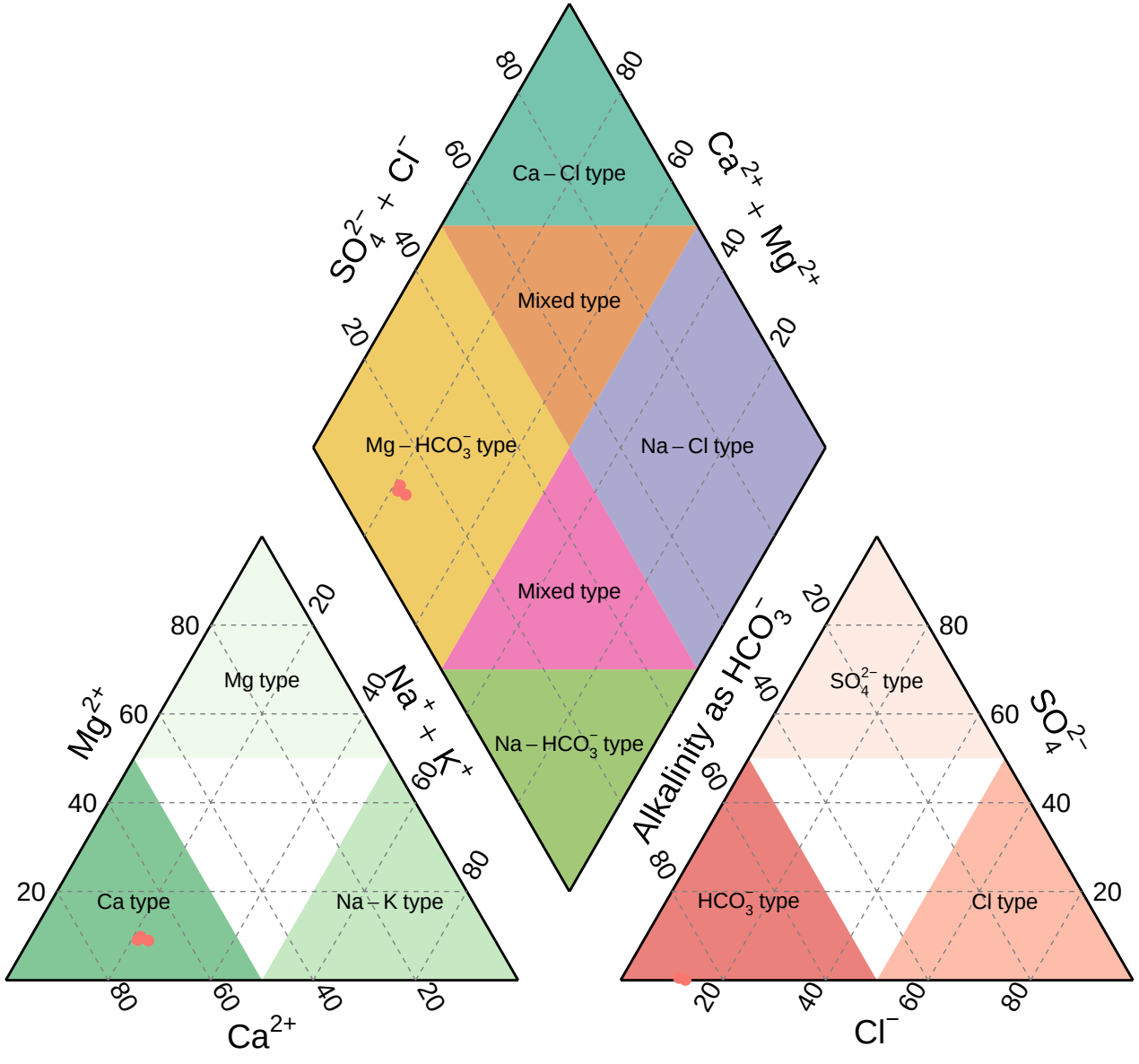
Location

- MW−35SB

Screen Geology

- Shallow Bedrock

Trilinear Plot of Groundwater Major Ion Chemistry: Well MW-36



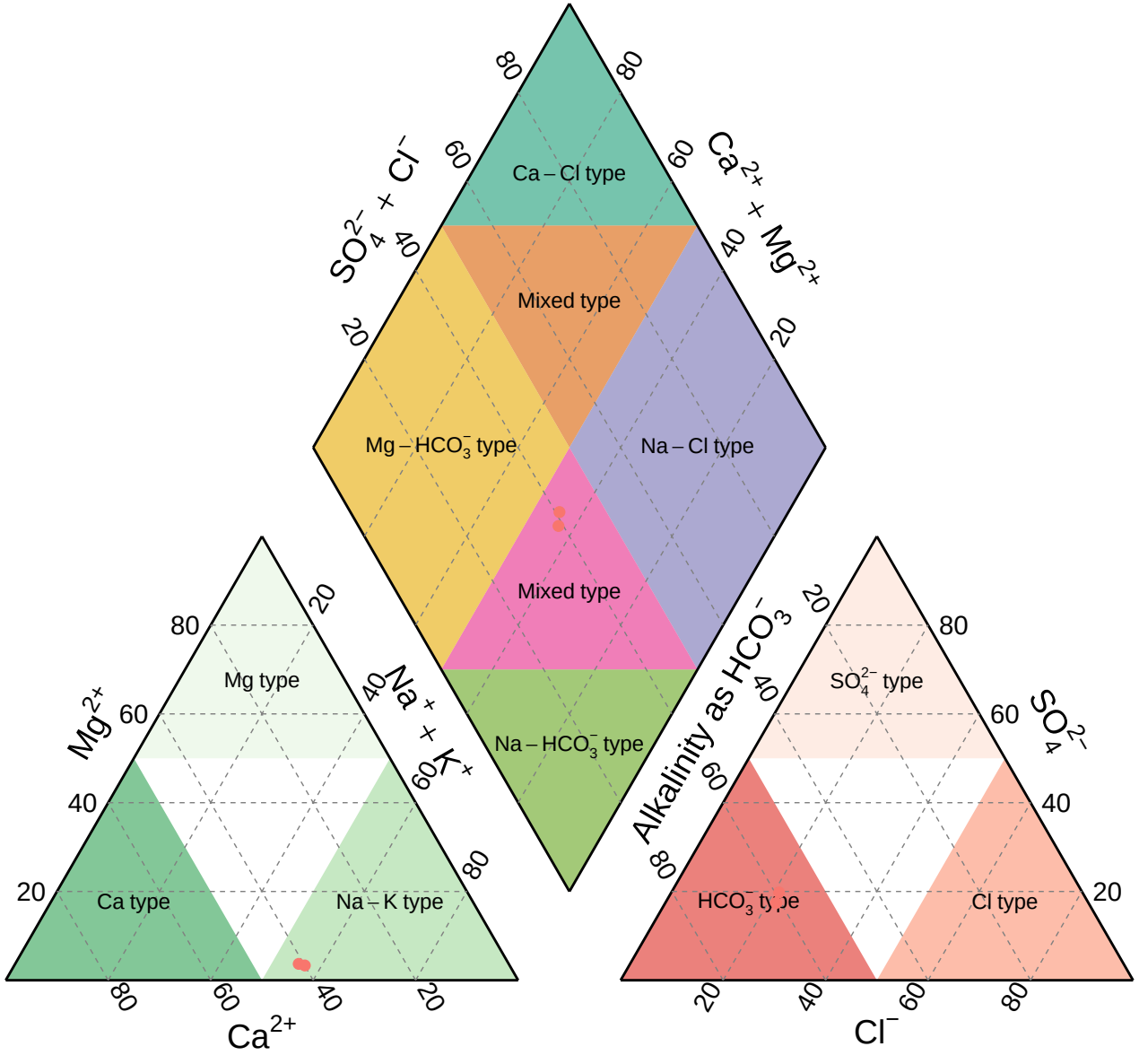
Location

- MW−36

Screen Geology

- Shallow Bedrock

Trilinear Plot of Groundwater Major Ion Chemistry: Well MW-41



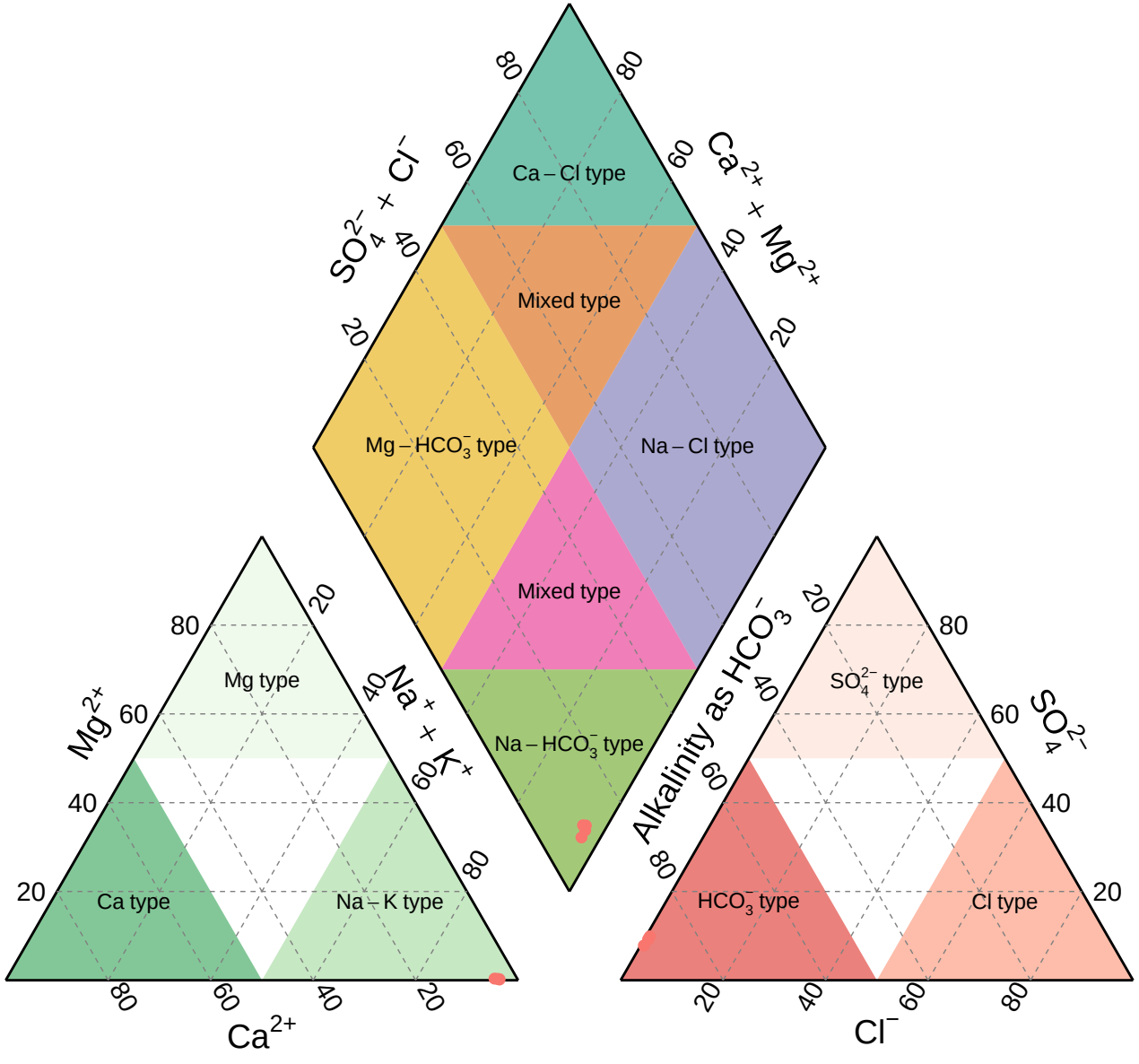
Location

- MW−41

Screen Geology

- Shallow Bedrock

Trilinear Plot of Groundwater Major Ion Chemistry: Well MW-42



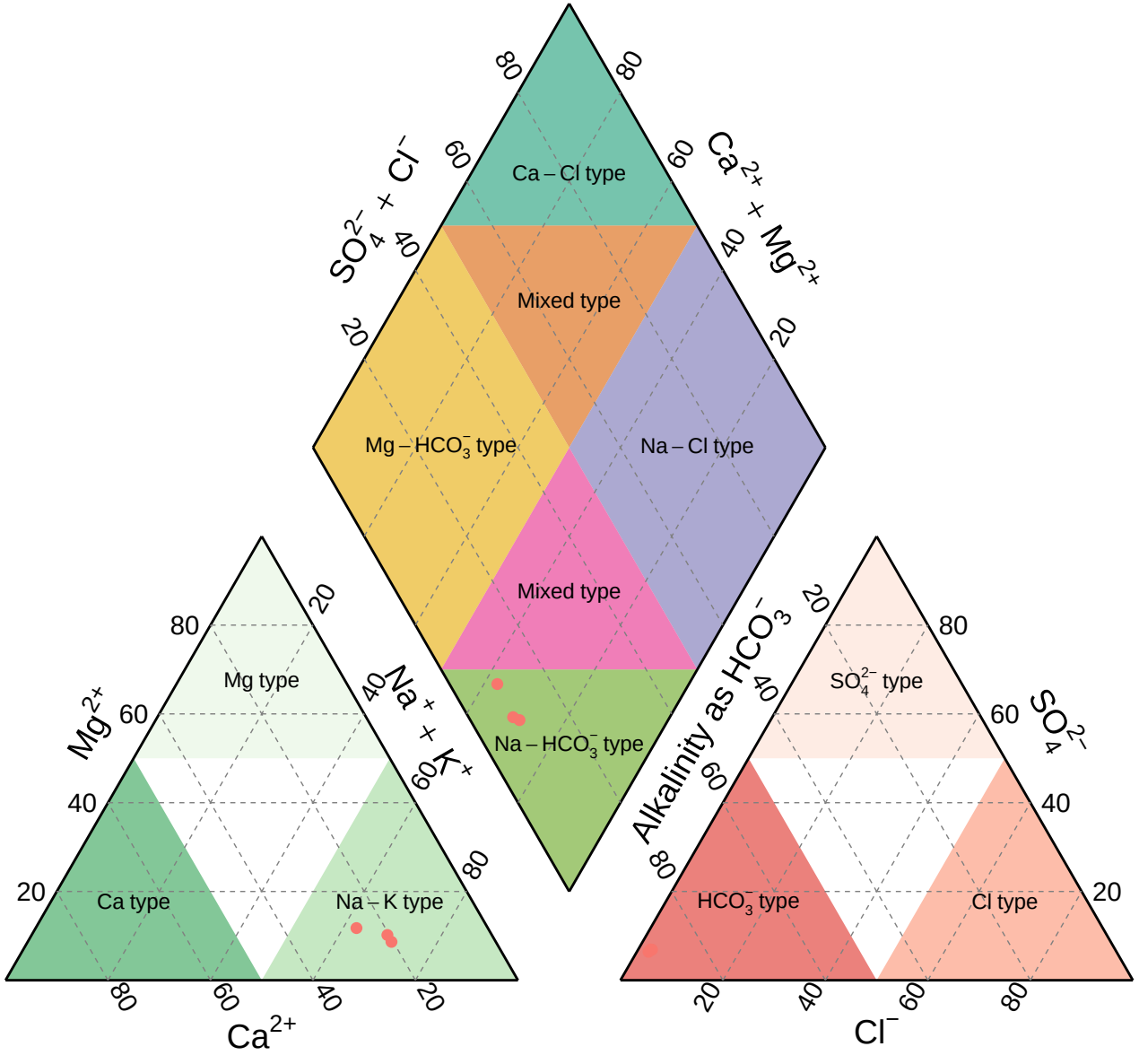
Location

- MW−42

Screen Geology

- Shallow Bedrock

Trilinear Plot of Groundwater Major Ion Chemistry: Well SMW-1



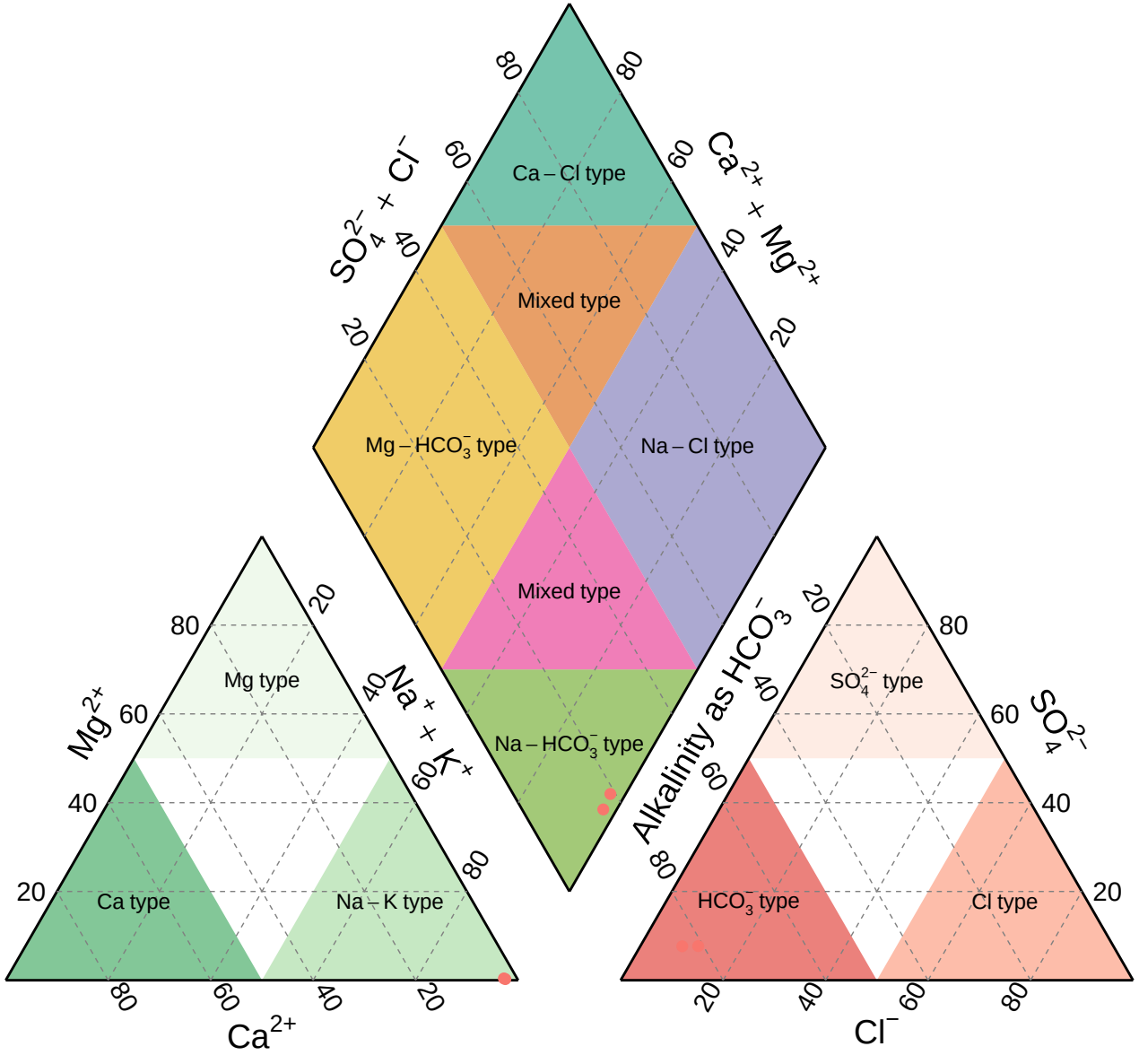
Location

- SMW−1

Screen Geology

- Overburden

Trilinear Plot of Groundwater Major Ion Chemistry: Well SMW-1SB



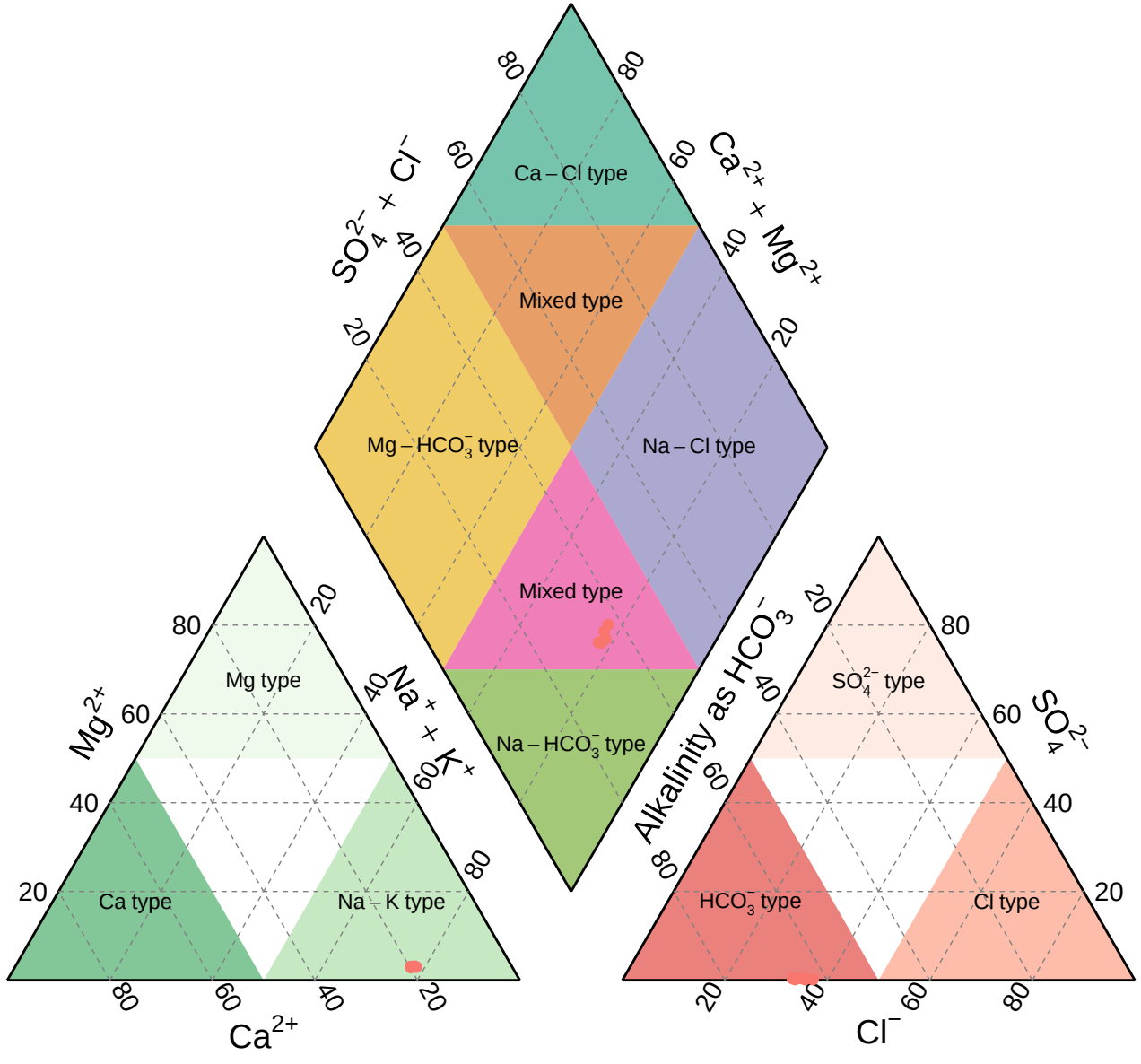
Location

- SMW−1SB

Screen Geology

- Shallow Bedrock

Trilinear Plot of Groundwater Major Ion Chemistry: Well SMW-3



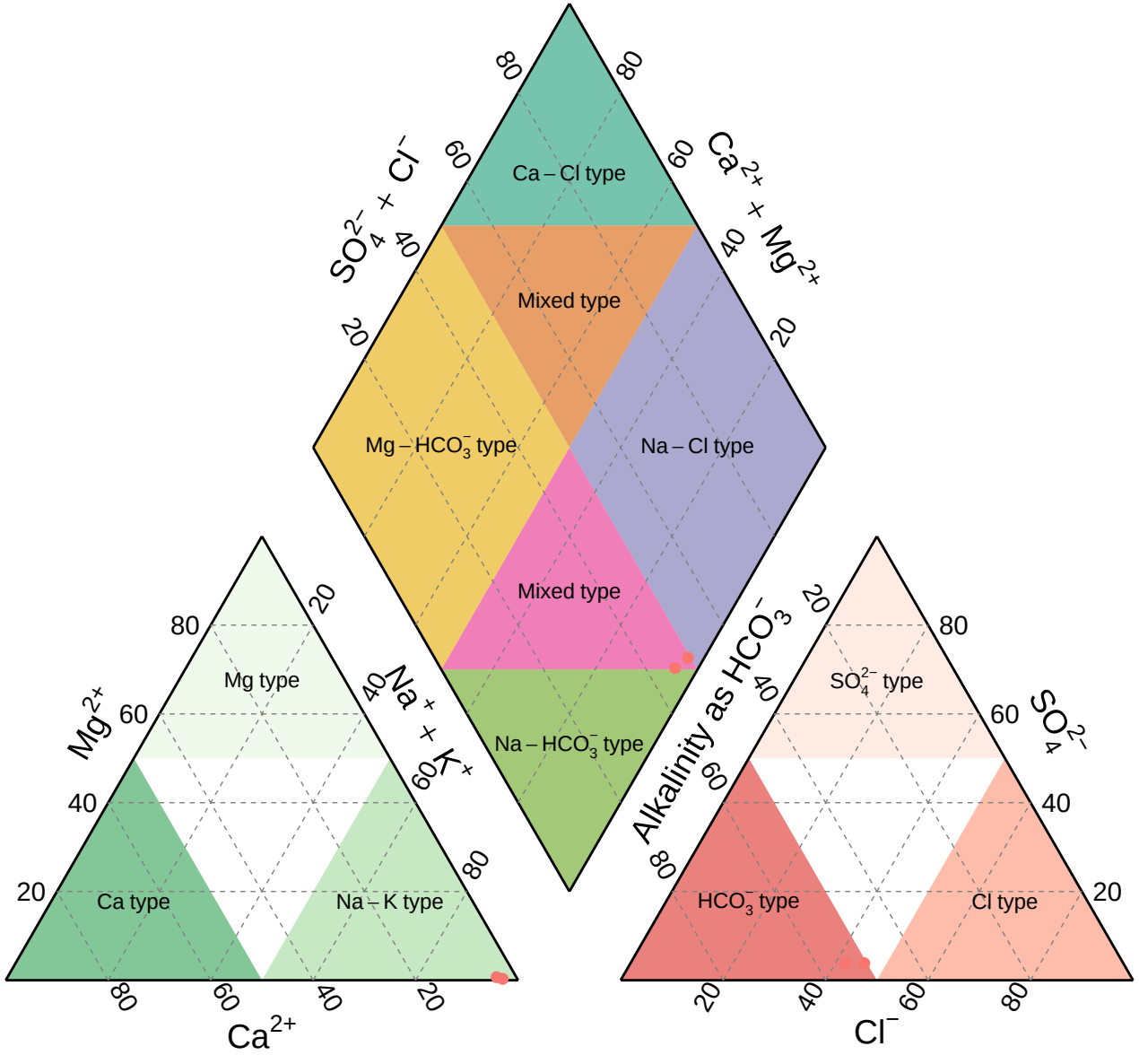
Location

- SMW−3

Screen Geology

- Overburden

Trilinear Plot of Groundwater Major Ion Chemistry: Well SMW-3SB



Location

- SMW−3SB

Screen Geology

- Shallow Bedrock

H-3

Project Quality Assurance Project Plan

Quality Assurance Project Plan



White Pine Copper LLC
White Pine, Michigan

August 2024

Project ID: 24W005

Solving our clients' toughest science and engineering challenges.

Quality Assurance Project Plan

Project ID: 24W005

Prepared for

White Pine Copper LLC

White Pine, Michigan

Prepared by

Foth Infrastructure & Environment, LLC

August 2024

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2121 Innovation Court • De Pere, WI 54115 • (920) 497-2500

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Quality Assurance Project Plan

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List of Abbreviations, Acronyms, and Symbols

%	percent
A2LA	American Association of Laboratory Accreditation
COC	chain of custody
CTL	Client Team Leader
DQO	data quality objectives
DUP	duplicate
EB	equipment blank
EDD	electronic data deliverable
FB	field blank
FBLL	field blank low-level
Foth	Foth Infrastructure & Environment, LLC
GW	groundwater
ICPMS	Inductively Coupled Plasma/Mass Spectrometry
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
MDL	method detection limit
MS	matrix spike
MSD	matrix spike duplicate
MSHA	Mine Safety and Health Administration
NIST	National Institute for Standards and Technology
ORP	oxidation reduction potential
OSHA	Occupational Safety and Health Administration
PM	Project Manager
QA	quality assurance
QAM	Quality Assurance Manual
QAPP	Quality Assurance Project Plan
QC	quality control
RL	reporting limits
RPD	relative percent difference
SOP	Standard Operating Procedure
SW	surface water
the Project	White Pine North Project
TOC	Total Organic Carbon
USEPA	United States Environmental Protection Agency
WPC	White Pine Copper LLC
WPM	White Pine Mine
WPN	White Pine North

1. Introduction and Project Management

White Pine Copper LLC (WPC) is a Joint Venture between Kinterra Capital and Highland Copper Company. WPC is seeking to develop the White Pine North (WPN) Project (the Project). The Project is located at the White Pine Mine (WPM) site within the historical Copper Range district of the Upper Peninsula of Michigan, in Ontonagon County, as shown on Figure 1-1.

The Project is proposing an underground mine targeting a mineralized area previously undeveloped by the WPM. The Project will expand the northern part of the existing tailings basin and will locate and develop a new mine portal and associated processing infrastructure. Mining at the WPM site has been conducted via underground methods since the late 1800s. Processing was done on site above ground and during the 1950s, a smelter was built, and on-site smelting took place. Mining and processing at the site ceased in 1997.

Collecting a robust and representative water chemistry baseline is critical to meeting permitting requirements, specifically two years of baseline analytical data, for forecasting potential impacts and for characterizing and contextualizing any future changes on site (e.g., operational monitoring). Quarterly sampling of water quality, water levels, and flows at monitoring wells and surface water locations will be conducted to satisfy two primary objectives:

- measure natural variations in water chemistry over time, and
- provide an additional line of evidence using groundwater geochemistry to infer flow paths and, by extension, areas of groundwater recharge and discharge.

In support of WPC's baseline data collection needs, Foth Infrastructure & Environment, LLC (Foth) has prepared this Quality Assurance Project Plan (QAPP). The QAPP describes the quality assurance/quality control (QA/QC) procedures that will ensure environmental baseline data collection provides representative, useable, and high-quality data to meet the data quality objectives (DQO) of groundwater and surface water quality collection.

1.1 Project Background

Two work plans, Groundwater Characterization and Monitoring Work Plan (Foth, 2024a) and Surface Water Monitoring Work Plan (Foth, 2024b) have been developed to support the Project's hydrological and hydrogeological data needs. These work plans provide Project background including the hydrological and hydrogeological Project setting. In addition, previously conducted hydrological and hydrogeological assessment are summarized within these work plans. These work plans contain information and directives relative to specific tasks that contribute to overall success of the Project. This QAPP supports the collection of baseline analytical monitoring data described in the work plans.

1.2 Project Team

This section describes the organization of the Project team, lists training and certification requirements for sampling personnel, describes documentation and recordkeeping procedures, and identifies lines of communication for the Project. The Project organization chart is illustrated on Figure 1-2.

1.2.1 Roles and Responsibilities

Client: White Pine Copper LLC
The WPC project manager, Amanda Zeidler, is responsible for implementing the Project and has the authority to commit the resources necessary to meet Project objectives and requirements. The primary function of the WPC project manager is to ensure technical and scheduling objectives are achieved

successfully. The WPC project manager may delegate some of these responsibilities to other individuals representing WPC.

Client Team Leader (CTL):
The CTL, Steve Donohue (Foth) will be responsible for planning and implementation of the Baseline Studies on behalf of WPC. They will be the primary contact at Foth for all matters concerning the performance and progress of the Project. Specific Project duties of the client team leader include:

- establishing Project direction and technical objectives; and
- client interaction.

Project Manager (PM):
The PMs, Jakob Wartman and Nick Glander (Foth), will be responsible for the completion of specific Project tasks and QC of Project deliverables. They will direct and coordinate the field team and subcontractors. They will report regularly to CTL on field progress. Specific Project duties of the PM include:

- directing and implementing Project activities;
- allocating staff resources to the Project;
- maintaining the Project schedule; and
- overseeing the preparation of Project deliverables.

Technical Lead:
The technical lead, Jed Chrestensen (Mannik & Smith Group, Inc.) will be primarily responsible for the coordination of field and laboratory activities, preparations supporting the sampling events, and developing event documentation. When sampling is underway, they will be in daily contact with the sampling team to report each day's progress and resolve any problems encountered. They are responsible for review and maintenance of Foth Standard Operating Procedures (SOP).

Chemistry QA Manager:
The Chemistry QA Manager will be in charge of field and laboratory data QA. They will be responsible for evaluating the quality of the field data, including review of field forms and logbooks. They will work with the Technical Lead to oversee equipment usage and training to support satisfactory data quality and documenting compliance with laboratory QA programs. They will also be responsible for the review and correction of laboratory sampling activities that do not meet industry standards, laboratory SOPs, analytical methods, or specific contractual agreements.

Health and Safety Coordinator:
The Health and Safety Coordinator will coordinate health and safety activities. They will be responsible for assuring that Foth staff involved in field activities has appropriate health and safety training in accordance with Mine Safety and Health Administration (MSHA) and Occupational Safety and Health Administration (OSHA) regulations, and WPC requirements. All Foth members of the Project team understand the special commitment to health and safety expected for the Project, and that effective promotion of health and safety requires daily attention and consideration of site conditions.

Laboratory: Eurofins TestAmerica
Eurofins TestAmerica will analyze all samples collected during this Project. Sandra Fredrick will serve as the Eurofins TestAmerica Project Manager and contact. The chemistry QA Manager will be responsible for executing delivery and schedule data review and attainment of DQO.

1.2.2 Personnel Certification

All sampling activities conducted will be performed by individuals who possess training and experience in the specific sampling and monitoring techniques. Individuals collecting samples will be trained, as needed, on the specific requirements provided in the field SOPs (Appendix A). Sampling personnel will have site-specific safety certifications and training as defined within the Groundwater Characterization and Monitoring Work Plan (Foth, 2024a) and Surface Water Monitoring Work Plan (Foth, 2024b).

1.2.3 Project Communication

The formal chain of communication for this Project will make information sharing efficient and comprehensive and keep the management team aware of activities and events. The field team will stay in close verbal or written contact with the PM, to keep them informed of any significant developments in the field or at the laboratories. QA reports to management include verbal status updates, data validation reports, and final laboratory reports.

1.3 Data Quality Objectives

DQOs determine requisite type of data, most appropriate data collection procedures, and define acceptable decision error limits with the objective of supporting Project goals and decision making. The use of a systematic planning process to define these quality objectives and performance criteria follows guidance by the United States Environmental Protection Agency (USEPA).

The objective for groundwater and surface water quality data collection at the Project is to define baseline conditions proximal to the Project, using data collection procedures that will ensure collection of representative data of known and acceptable quality. The data will be used to support decision making and other intended future uses of the data.

1. **State the Problem.** Groundwater and surface water quality is required to establish baseline concentrations for the Project.

2. **Identify the Goals.** Tasks include groundwater data collection and surface water data collection. The goal of data collection is to establish baseline concentrations.

3. **Identify the Information Inputs**. Numerous data collection programs have taken place at the Project site with previous work being summarized in the Groundwater Characterization and Monitoring Work Plan (Foth, 2024a) and Surface Water Monitoring Work Plan (Foth, 2024b). These work plans also hydrogeological and hydrological data to be collected as part of the current sampling program.

4. **Define the Boundaries of the Study**. The Project area is defined on Figure 1-1.

5. **Develop Analytical Approach**. The analytical requirements are established to meet the primary Project goals stated in Step 2. Samples will be analyzed for different analytes depending on matrix and objectives to be met. Analytical detection limits are established to facilitate Project decisions and information for future use. The analytical approach and detailed analytical specifications are spelled out in Sections 3 and 4 of this QAPP.

6. **Specify Performance or Acceptance Criteria**. All measured data includes some level of uncertainty. The performance criteria and degree of uncertainty acceptable for this Project include defined precision, accuracy, representativeness, comparability, and sensitivity. These criteria are evaluated by applying the following QC requirements:

a. **Field QC**: Proper sampling procedures are described in the field SOPs and include field duplicate samples, and field and equipment blanks.

b. **Laboratory QC**: Laboratory QC procedures are described in this QAPP and also in supporting SOP for each method as supplied by the analytical laboratories and include QA/QC and acceptance criteria around method detection limits (MDL), reporting limits (RL), method blanks, laboratory control samples (LCS), matrix spikes/matrix spike duplicates (MS/MSD), and laboratory blanks. These QC and acceptance criteria are described in more detail in Section 4 of this QAPP.

7. **Develop the Plan for Obtaining Data.** The plan for data collection is the primary subject of this QAPP and field SOPs. The basis of the sampling design, rationale for sampling tasks, and scope of work are described in the Groundwater Characterization and Monitoring Work Plan (Foth, 2024a) and Surface Water Monitoring Work Plan (Foth, 2024b).

1.3.1 Sample Collection and Analyses Objectives

The objective of sample collection and analysis activities is to provide representative and defensible information on ambient surface water and groundwater conditions.

1.3.2 Quality Assurance/Quality Control Objectives

The use of standard methods and controlled systems during the collection and analyses of samples will help ensure data quality. Sample collection data quality will be maintained through the use of standard collection methods and equipment, field log books, and chain of custody (COC) forms. Analytical data QC will be achieved by using standard analytical methods for which SOPs (Appendix C) and analytical protocol specifications have been established, where applicable. The control and evaluation of errors due to possible matrix interference will be accomplished through the use of standard QA/QC methods such as MSs, blanks, and field duplicates.

1.3.3 Project Tasks and Schedule

The baseline studies will proceed in accordance with the Groundwater Characterization and Monitoring Work Plan (Foth, 2024a) and Surface Water Monitoring Work Plan (Foth, 2024b).

The anticipated schedule for the tasks described in this QAPP are shown below.

Task	Schedule
Field and Laboratory Groundwater Monitoring	Refer to Table 11 in the Groundwater Monitoring Work Plan[1]
Field and Laboratory Surface Water Monitoring	Refer to Table 3 in the Surface Water Monitoring Work Plan[2]

Notes:
[1] Foth, 2024a
[2] Foth, 2024b

2. Field Data Acquisition and Generation

This section of the QAPP describes the organization and responsibilities for field sampling activities and the associated data acquisition and generation.

2.1 Field Sample Acquisition

SOPs Referenced (located in Appendix A)

- SOP 3207 – Field Log Book

Field data, including visual observation, manual measurement, and measurements made by field instrumentation will be recorded in field log books or forms and then entered into an electronic data file by a field team member after the completion of the field event and stored electronically in the Project file. The Field Task Lead and Chemistry QA Manager will review the data for consistent adherence to the QAPP. Any concerns resulting from data review will be discussed with the PM and corrected, if possible, and incorporated into data evaluation process.

Field data calculations, transfers, and interpretations will be reviewed by the Technical Lead, Chemistry QA Manager, or PM for accuracy and agreement. Field documentation, data reduction, and accuracy of data entries into the data log will be checked for the following: completeness, readability, use of appropriate procedures and standard protocol, appropriate instrument calibration and maintenance records, correctness of sample locations, reporting units, calculations and interpretations, and reasonableness of data collected. Should sampling procedures or plans be modified, changes need to be clearly stated and decision justifications/reasoning recorded.

The PM will maintain records that document all activities and data related sampling and analysis. Once field work is complete, the hard copies (where applicable) and scanned electronic copies of these documents will be maintained in Foth's master Project file. The Project files will be retained for at least 15 years from the date the Project is closed.

2.1.1 Groundwater Sampling

SOPs Referenced (located in Appendix A)

- SOP 2020 – Low-Level Mercury Groundwater Sampling
- SOP 2051 – Groundwater Purging & Sampling – Fixed Volume
- SOP 2201 – AquaTroll® 600 Multiparameter Sonde

The groundwater sampling program at each well is summarized in the Groundwater Characterization and Monitoring Work Plan (Foth, 2024a). There are currently 23 groundwater monitoring locations, with six additional locations planned for installation and subsequent sampling (Figure 2-1).

Groundwater quality monitoring is conducted to quantify baseline groundwater quality for constituents of interest, including field parameters, general chemistry, major cations and anions, metals, redox sensitive parameters, and other constituents. Field parameters to be recorded include pH, specific conductance, temperature, dissolved oxygen, oxidation reduction potential (ORP), and turbidity. The water quality analytical parameter list, associated methods, laboratory standard sample containers, preservatives, and hold times are presented in Table 2-1.

This sampling procedure will also use the water quality in-situ parameters to identify when a well has stabilized during purging as an indicator to begin sampling. These parameters and tolerances are located in Table 2-2. Example forms for field observations are provided with the SOPs.

Groundwater sampling protocols defined within the Groundwater Characterization and Monitoring Work Plan (Foth, 2024a) consist of:

- Gauging monitoring well network for water levels;
- Pumping of selected monitoring wells prior to sampling;
- Collecting the field parameters (specific conductivity, temperature, pH, ORP, and turbidity); and
- Collecting groundwater samples for laboratory analysis.

2.1.2 Surface Water Sampling

SOPs Referenced (located in Appendix A)

- SOP 2021 – Low-Level Mercury Surface Water Sampling
- SOP 2062 – Surface Water Sampling – Sampling from Shore
- SOP 2101 – Stream Flow Site Selection Criteria & Measurement with Velocity-Area Method
- SOP 2102 – Stream Flow Measurement Using Flowtracker 2 ADV
- SOP 2103 – Stream Flow Measurement Using ADCP
- SOP 2106 – Stage-Discharge Relation for Open Channel Flow
- SOP 2107 – Staff Gauge Installation and Water Level Monitoring
- SOP 2201 – AquaTroll® 600 Multiparameter Sonde

The surface water sampling program refers to stream flow monitoring and surface water quality monitoring, and the program is summarized in the Surface Water Monitoring Work Plan (Foth, 2024b). Flow monitoring will be performed at 18 existing locations and two additional proposed locations as shown on Figure 2-2, using a combination of continuous and manual flow monitoring techniques.

Water quality monitoring will occur at 18 existing and two additional proposed stream flow locations. In addition, water quality monitoring will occur at two existing Lake Superior locations, four existing ponded locations, and two additional proposed ponded locations as described in the Surface Water Monitoring Work Plan (Foth, 2024b) and shown on Figure 2-2.

Surface water quality monitoring is conducted to quantify baseline surface water quality for constituents of interest, including field parameters, general chemistry, major cations and anions, metals, and other constituents. Field parameters to be recorded include pH, specific conductance, temperature, dissolved oxygen, ORP, and turbidity. The surface water quality analytical parameter list, associated methods, laboratory standard sample containers, preservatives, and hold times are presented in Table 2-3.

Surface water sampling protocols defined within the Surface Water Monitoring Work Plan (Foth, 2024b) consist of:

- Retrieving continuous flow logger data and measuring surface water flow manually;
- Collecting the field parameters (specific conductivity, temperature, pH, ORP, and turbidity); and
- Collecting surface water samples for laboratory analysis.

2.2 Sample Identification

A sample numbering system identifies each sample including QA/QC samples. The sample code will provide a unique identifier for each sample, required by EQuIS data management software. Each sample, regardless of analytical protocol, also will be assigned a site-specific identification, which will contain the specific location identifiers to indicate where the sample was obtained. The site-specific identification is based on the following system: Sample Location Code_yyyymmdd. For example, a sample collected on

June 1, 2024, at surface water location PRC-01 would be assigned a sample identification of PRC-01_20240601.

Duplicate (DUP) samples will be identified using the following system: DUP-number-matrix_yyyymmdd, where number will be two numeric digits starting at 01 and increasing by one for each subsequent sample assigned sequentially for the sampling event, and matrix will be groundwater (GW) or surface water (SW). For example, the first duplicate sample collected as part of a groundwater monitoring event on June 1, 2024, would be assigned a sample identification of DUP-01-GW_20240601. Field blank (FB) and equipment blank (EB) samples will be identified using the same system as for duplicates, except DUP will be replaced with FB or EB (e.g., FB-01-GW_20240601).

Field blank low-level (FBLL) mercury will be collected at all locations where a low-level mercury sample is obtained. When a FBLL sample is collected, FBLL will be added onto the end of the sample identification. For example, a FBLL collected with sample PRC-01_06012024 will be assigned a sample identification of PRC-01_20240601_FBLL.

Sample Documentation
Field documentation will include sample labels, COC forms, and field forms and log books, SOPs are included in Appendix A. data validation information will be recorded to the EQuIS database, electronic copies of field forms, and field log books will be archived in the Project Master File on ProjectWise.

2.3 Field Quality Assurance and Quality Control Procedures

Field QA and QC are accomplished by QA/QC samples in accordance with industry standards. QA/QC samples will be analyzed as part of the overall laboratory QA/QC program. Results from the QA/QC samples will be reviewed prior to approval of the set of results from the sampling event. An overview of the purpose of various QA/QC samples is provided below.

SOPs Referenced (Located in Appendix A)

- SOP 3113 – Data Verification, Validation, and Qualification
- SOP 3260 – Shipping and Packaging of Non-Hazardous Samples
- SOP 3270 – Sample Chain of Custody

2.3.1 Quality Assurance

Analytical data will be submitted in accordance with the laboratory contract. The Chemistry QA Manager will review the field and laboratory data, assess field sample precision, check data set completeness, and assess overall usability of data for the intended purpose. Limitations of data usability and deviations from this QAPP will be evaluated and reported.

Field data, including visual observation, manual measurements, and measurements made by field instrumentation will be recorded in field log books or forms and then entered into an electronic data file after the completion of the field event and stored electronically in the Project file.

Field data calculations, transfers, and interpretations will be reviewed for accuracy and agreement. Field documentation will be checked for the following: completeness, readability, use of appropriate procedures and standard protocols, appropriate instrument calibration and maintenance records, correctness of sample locations, reporting units, and reasonableness of data collected. Should sampling procedures be modified, changes need to be clearly stated and decision justifications recorded.

2.3.2 Sample Containers and Preservation Requirements

Sample containers and preservation requirements are listed for groundwater in Table 2-1 and surface water in Table 2-3. Samples requiring refrigeration will be stored in an ice chest containing sufficient wet ice for transport to the laboratory. Samples requiring pH adjustment will be preserved on site through the use of laboratory provided preserved sample bottles. Preservatives will be provided by Eurofins Test America and shall be of sufficient purity so as not to interfere with the analysis of the parameters of interest. The laboratory shall verify the pH of preserved samples upon receipt.

2.3.3 Sample Handling Custody, Transport, and Receipt

Collected samples will be handled and analyzed in a consistent manner to assure data quality. The following subsections provide the methodology for sample handling, shipping, and laboratory analysis.

Sample Packaging and Chain of Custody
Sample packaging procedures are designed to ensure collected samples and their accompanying COC will arrive at the laboratory intact, sealed, and identified.

Samples must arrive to laboratory within allowed temperature (0 to 6°Celcius) and will be packaged in coolers with ice and temperature blanks, where applicable, as described in the SOP.

All water samples collected for analytical laboratory analysis will be handled using the COC procedures in the SOP in Appendix A. Example COC forms are provided in Appendix A and will be initiated during sample collection. COC forms will contain the samples identification number, sample date and time, sample matrix, sample type, preservation, and analyses required. The original COC, with appropriate relinquishment signatures, will accompany the samples to the laboratory within the sample shipping coolers.

Sample Shipment/Delivery
All samples will be sent to the appropriate analytical laboratory using overnight courier such as FedEx® or a laboratory contracted courier. The Project SOP for sample shipment is provided in Appendix A.

Prior to shipping the samples, the laboratories will be notified of the expected receipt date and time to assure the laboratory is prepared to receive the samples. Samples collected for general chemistry and metals analysis will be sent to Eurofins Test America using the following address:

Eurofins Chicago
2417 Bond Street
University Park, IL 60484 USA
Phone: 920-261-1660

2.3.4 Field Quality Control Samples

This section addresses the calibration and preventive maintenance of field equipment.

Field QA will consist of the use of standard procedures and processes to complete field activities. Field QC will consist of checking instrument calibrations and collection of QC samples. The following subsections describe the field QA/QC processes.

Field Equipment Calibration
Dissolved oxygen, pH, oxidation-reduction potential, conductivity, turbidity and temperature, measurements will be collected in the field using direct-reading meters. Instruments must be properly calibrated to produce technically valid data. Documented calibration and calibration check results verify that the instruments used for measurement are in proper working order and the data produced are

reliable. Daily calibration is necessary to support the DQOs for this Project. Documented calibrations are necessary to ensure that the data are technically and legally defensible. Each meter will be calibrated and operated in accordance with the manufacturer's instructions. In general, the following information will be recorded to document the calibration:

- name of device/instrument;
- instrument serial and/or identification number;
- frequency of calibration;
- date of calibration;
- results of calibration;
- name of person performing the calibration; and
- identification of calibration gases/solutions (if applicable).

Field calibration records will be maintained in the Project file.

Preventive Maintenance
The Field Team Leader is responsible for documenting the maintenance of field equipment prescribed in the manufacturer's specifications. Scheduled maintenance will be performed by trained personnel. Any subcontractors shall be responsible for maintenance of equipment needed to carry out subcontracted duties.

2.3.4.1 Duplicate Samples

Blind duplicate samples are used to test for sampling and analytical reproducibility (i.e., precision). Blind duplicate samples will be collected by alternatively filling a primary set and secondary set of laboratory containers as close in time as practical. The parent sample of the blind duplicate sample will be recorded in the field book. Blind duplicate samples will be assigned an identification alias (e.g., DUP-01-GW_20240601) on the sample bottle label and on the COC sheet to avoid alerting laboratories of the parent sample. A relative percent difference (RPD) calculation will be performed between the primary (i.e., parent) and duplicate sample. Blind duplicate samples will be collected at a frequency of one blank per 20 primary samples.

2.3.4.2 Field Blanks

Field blanks are used to detect potential background or method contamination. Field blanks will be analyzed for target analyte(s). Sample containers used for field blanks will be of the same type and preservative as the primary sample container for the target analyte. Laboratory-controlled, target analyte-free water will be used to fill the field blank sample container.

For low-level mercury sampling, field blanks will be collected at the frequency of one blank per primary sample. For other analyte(s), field blanks will be collected at a frequency of one blank per 20 primary samples (approximately 5 percent [%] of the number of samples).

Low-level mercury sampling will be conducted as described in the SOPs provided in Appendix A. "Dirty Hands/Clean Hands" method will be used to collect low level samples. The critical procedures for collecting these samples are summarized below.

1. The "Dirty Hands" worker is responsible for sample equipment preparation, operation of any machinery and any other non-direct sampling activities.

2. The "Clean hands" worker is limited to any operations involving contact with the sample bottle, transfer of sample from collection device and associated inner packaging for sample bottles.

2.3.4.3 Equipment Blanks

Equipment blanks are used to detect potential cross-contamination resulting from inadequate decontamination procedures. Equipment blanks will be collected when non-dedicated sampling equipment is used at multiple sample locations. Equipment blanks will be collected following method required decontamination procedures. A minimum of one equipment blank per analytical batch per method per every 20 primary samples (approximately 5% of the number of samples) will be collected and analyzed.

2.4 Corrective Action

Project assessment and oversight may take place during Project implementation through field performance audits, if deemed necessary by the client or Foth PM. It is anticipated that field inspections would be conducted by a designee of the Foth PM. Depending upon the tasks at hand, field inspections may involve the review and evaluation of:

- implementation of approved work procedures;
- sampling procedures;
- sampling documentation;
- labeling, packaging, storage, and shipping of samples;
- completion of field records; and
- QC compliance.

Field records will also be reviewed to verify that field-related activities are performed and documented in accordance with the QAPP. Items to be reviewed include, but are not limited to:

- field activity logs;
- collection forms;
- custody transfer forms and/or COC forms; and
- field measurement records.

Preliminary results of the inspections will be reviewed with the PM to ensure that deficiencies adversely affecting data quality are immediately corrected. If the need for corrective action is identified, then the necessary actions will be immediately implemented, with the steps taken documented. Subsequent inspections will be conducted to ensure that correct procedures are followed. The findings of the field inspection, as well as any corrective actions, will be included in the sampling event memorandum.

2.5 Project Variance Contingencies

The objective of the Project variance contingency plan is to provide a process that documents and allows for deviations from procedures outlined in this QAPP, or amendments to this QAPP, in order to improve Project data quality. This Project variance contingency allows the Project director, or designee, to authorize and document necessary changes, in field or laboratory procedures, discovered during implementation of this QAPP. Authorized changes will be tracked in the Project Variance Contingency Form (Appendix B). The form will display the authorizing signature, the prescribed method, the new method, and summarize the reason or basis for the change. This form will be maintained in the Project file.

3. Laboratory Analysis Plan

The contract laboratory Eurofins Test America is certified under National Environmental Laboratory Accreditation Program. Relevant certifications are included in Appendix C. The laboratory will document all activities and results related to sample analysis. Internal laboratory documentation procedures are described in the applicable laboratory Quality Assurance Manual (QAM), which are attached in Appendix C and within laboratory SOPs (Appendix D). Quantitation procedures specified for each method must be followed, and data should be reported to the detection limit. If data are reduced manually, the documentation must include the formulas used. Any application software used for data reduction must have been previously verified by the laboratory for accuracy. Documentation of the software's verification must be maintained on file in the laboratory. Documentation of data reduction must allow recreation of the calculation.

Level 2 data reports are required to be reported within 10 days of receipt of the last sample in each sample batch. Electronic data deliverables will be compatible with Foth's EQuIS format.

All analytical data will undergo review at the laboratory before release including:

- The analyst performing the test initially will review 100% of the data to check for the following:
  - Sampling preparation information is correct and complete.
  - Sample analysis information is correct and complete.
  - Appropriate analytical procedures were followed.
  - Analytical results and reporting units are correct and complete.
  - QC samples are within established control limits or qualified when outside limits.
  - Documentation is complete.

- The senior analyst or the section supervisor will review 100% of the data for the following:
  - Accuracy and compliance with calibration and QC requirements, holding-time compliance, and completeness.
  - Verification of analyte identification and quantitation.
  - Comparison of calibration and QC results with the applicable control limits.

- The Laboratory Project Manager is responsible for:
  - Review of the RL to see that they meet the Project objectives.

Each data package will include all the information required for a complete QA review and at least the following information (when applicable):

- Case narrative that describes sample types, tests performed, problems encountered, corrective actions taken, and general comments.

- COC and sample receiving documentation.

- Analytical data summary reported by sample and test. Pertinent information for these samples, such as dates sampled, received, prepared, or extracted, should be included on each page. The practical quantitation limit and MDL for each analyte must also be provided. In addition to a hard-copy report or PDF copy of the report, laboratories will provide an electronic data deliverable (EDD).

- Results of laboratory performance and QC samples, including LCS recoveries analyzed with the data set, as applicable, listed together with the control limits; the analytical results for method blanks and calibration blanks generated during analysis of inorganic parameters; laboratory

duplicate results together with RPD control limits; results of any field sample duplicates, MS\MSDs along with the specific laboratory acceptance criteria; internal standards.

- Sample preparation and cleanup logs, including preparation batch and analytical batch associations.

- Initial and continuing calibration data, including instrument printouts and quantification summaries for all analytes. All the pertinent standards information and traceability and standard log book information for individual standards solutions. Instrument tuning check data.

- Any correspondence that occurred between the laboratory and the client regarding sample issues will be summarized in the case narrative.

Analytical data will be submitted in accordance with the laboratory contract. The Chemistry QA Manager will review the field and laboratory data, assess field sample precision, check data set completeness, and assess overall usability of data for the intended purpose. Limitations of data usability and deviations from the QAPP will be evaluated and reported. Foth will maintain data packages and EDD for all analyses.

Analytical data will be transferred directly from the instrument to a computerized data system whenever possible. Raw data will be stored electronically. Laboratory data entry will be sufficient to document information used to arrive at reported values. Data will be stored electronically in WPC's database.

3.1 Laboratory Analytical Parameters

Groundwater and surface water samples will be analyzed for the parameters listed in Tables 3-1 and 3-2, respectively. Laboratory standard sample containers, preservatives, and hold times are also presented in Tables 3-1 and 3-2.

3.2 Laboratory Analytical Method Requirements

After samples are received by the laboratory, they will be analyzed by methods listed in Tables 3-1 and 3-2, with quantification limits as listed. Analytical preparation methods and procedures to be performed will be in accordance with the laboratory QAM (Appendix C) and SOPs (Appendix D).

3.3 Laboratory Quality Assurance

Laboratory QAMs Referenced (Located in Appendix C)

- QA Manual – Chicago, IL
- QA Manual – Tacoma WA

Laboratory SOPs Referenced (Located in Appendix D)

- Ammonia by Flow Injection Analysis
- Analysis of Metals by Inductively Coupled Plasma/Mass Spectrometry (ICPMS)
- Determination of Inorganic Anions by Ion Chromatography
- Determination of Solids in Waters and Wastes
- Free and Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry
- Phosphorus: Total, Ortho, and Organic
- Preparation and Analysis of Methyl Mercury by Gas Chromatography with Cold Vapor Atomic Fluorescence Detection
- Preparation and Analysis of Mercury in Aqueous and Solid Samples by Cold Vapor Atomic Fluorescence

- Salinity by Calculation, Electrical Conductivity
- Sulfide
- Total Organic Carbon (TOC)
- Total, Carbonate, Bicarbonate, and Hydroxide Alkalinity

This section presents QA/QC requirements relevant to analysis of samples that will be followed during Project analytical activities. The laboratory QAM (Appendix C) and laboratory SOPs are provided (Appendix D). The purpose of the QA/QC program is to produce data of known quality that satisfy the Project objectives and meet or exceed the requirements of the standard methods of analysis.

The chemical data to be collected for the baseline studies will be used to evaluate baseline conditions. As such, it is critical that the chemical data be of the highest confidence and quality. Consequently, strict QA/QC procedures will be adhered to. These procedures include the following:

- adherence to strict protocols for field sampling and decontamination procedures;
- collection and laboratory analysis of appropriate blanks to monitor for interference and/or contamination;
- collection and laboratory analysis of MS, MSD, and blind duplicate samples to evaluate analytical precision and accuracy; and
- attainment of completeness goals.

Standard material used in a calibration and to prepare samples will be traceable to National Institute for Standards and Technology (NIST), USEPA, or an equivalent source. The standard materials will be current.

Supplies will be visually inspected prior to their use in the field or laboratory. A current inventory and appropriate storage system for these materials will ensure their integrity prior to use. Efficiency and purity of supplies will be monitored through the use of standard materials and blank samples.

Sample preparation and analysis will be completed within the required method holding time. Holding time begins at the time of sample collection. If holding times are exceeded and the analyses performed, the associated results will be qualified as described in the applicable validation procedure. The following definitions of extraction and analysis compliance are used to assess holding times:

- preparation or extraction completion – completion of the sample preparation process as described in the applicable method, prior to any necessary extract cleanup; and
- analysis completion – completion of all analytical runs, including dilutions, second-column confirmations, and any required reanalysis.

3.3.1 Method Blanks

Blanks are used to monitor each preparation or analytical batch for interference and/or contamination from glassware, reagents, and other potential contaminant sources within the laboratory. A method blank is an analyte-free matrix (laboratory reagent water for aqueous samples). The blank is run through the entire sample preparation and analytical process, along with the samples in the batch. At least one method blank should be used per preparation or analytical batch. If a target analyte is found at a concentration that exceeds the RL, corrective action must be taken to identify and eliminate the contamination source. All associated samples must be re-prepared and/or re-analyzed after the

contamination source has been eliminated. No analytical data may be corrected by the laboratory for the concentration found in the blank.

3.3.2 Matrix Spike/Matrix Spike Duplicate

An MS is used to determine the effect of the sample matrix on compound recovery for a particular method. The MS/MSD set consists of the sample matrix that is then spiked with known concentrations of all known target analytes. The MS and MSD are evaluated against the method or laboratory derived criteria. If compound is outside control limits, it must be qualified appropriately.

A MS/MSD will be processed once every 20 samples for this Project.

3.3.3 Laboratory Control Samples

The LCS is used to evaluate the performance of the entire analytical system including preparation and analysis. An LCS consists of a matrix similar to the associated sample and is free of analytes of interest and spiked with known concentrations of all target analytes. The LCS is evaluated against the method default or laboratory-derived acceptance criteria. The number of allowable exceedances depends on the number of compounds in the LCS. If exceedances are greater than allowable limit, an analytical batch may be qualified.

An LCS is processed at a minimum frequency of one per preparation batch, or if a method has no separate preparation step, an LCS will be processed with no more than 20 samples of a specific matrix performed by the same analyst, using the same method, standards, and reagents.

3.3.4 Laboratory Duplicates

A sample duplicate is a second portion of sample prepared and analyzed in the laboratory. It is used to measure the precision associated with preparation and analysis. The sample and duplicate are evaluated against the method or laboratory derived criteria for RPD. Any duplicate outside these limits must be qualified appropriately.

A sample duplicate will be processed once per event or one per every 20 samples for this Project.

3.4 Laboratory Quality Control Practices

3.4.1 Instrument Calibration

Analytical instruments will be calibrated in accordance with the procedures specified in the applicable method. Calibrations establish the dynamic range of an instrument, generate response factors used for quantitation, and demonstrate instrument sensitivity. All analytes that are reported will be present in the initial and continuing calibrations, and these calibrations must meet the acceptance criteria specified in the reference method. Records of standard preparation and instrument calibration will be maintained. Records shall unambiguously trace the preparation of standards and their use in calibration and quantitation of sample results.

Calibration of laboratory instruments is required to ensure that the analytical system is operating correctly and functioning at the proper sensitivity to meet established detection limits. Each instrument is calibrated with standard solutions appropriate for the type of instrument and the linear range established for the analytical method. Each method contains requirements for the number and concentration of calibration standards, which are described in the laboratory's QAM and SOPs. Each calibration is verified through the use of statistical tests, continuing calibration verification standards and blanks, LCS/laboratory control sample duplicate (LCSD), and blank spikes prior to the sample results being approved.

3.4.2 Instrument Performance Checks and Confirmation Analysis

Confirmation analysis must be carried out as specified for specific methods when the result is at or above the RL. The result designated as the primary result will be reported but may be reported from the confirmation column if there is a confirmed positive bias from interference on the primary column.

The laboratory will follow its specific SOP on reporting confirmation data, and in all cases, confirmation data will be clearly annotated in the data package during such an occurrence. All calibration and QC requirements must be met when confirmation analysis is performed.

3.4.3 Preventive Maintenance

Preventive maintenance procedures are essential to ensure reliable operation of laboratory equipment and instruments with minimal downtime. The frequency of routine preventive maintenance procedures should follow instrument manufacturer recommendations or be performed on an “as needed” basis. The analytical laboratory is responsible for analytical equipment calibration and maintenance as described in the laboratory QAM, Appendix C.

Analytical instruments testing, inspection, maintenance, setup, and calibration shall be conducted in accordance with analytical methods as described in laboratory SOPs and method specific criteria. Preventive maintenance within the laboratory will be the responsibility of the laboratory personnel and the analysts. At a minimum, the preventive maintenance schedules contained in the USEPA methods and laboratory SOPs, as well as those in the equipment manufacturer’s instructions, will be followed. This includes routine care and cleaning of instruments, as well as inspection and monitoring of the carrier gases, reagents, solvents, reference materials, and glassware used in analysis.

3.4.4 Hold Time Compliance

Sample preparation and analysis must be completed within the method-required holding times. The holding time for a sample begins at the time of sample collection.

3.4.5 Control Charts

Control charts are used to track the performance of laboratory control sample recoveries over time. These charts are useful in identifying trends and problems in an analytical method.

3.4.6 Standard Materials

Standard materials used in calibration and to prepare samples will be traceable to NIST, USEPA, American Association of Laboratory Accreditation (A2LA) or other equivalent approved source.

3.4.7 Supplies and Consumables

The laboratory will inspect supplies and consumables prior to their use in analysis. The materials description in the methods of analysis shall be used as a guideline for establishing the acceptance criteria for these materials.

3.5 Data Review

Data review is an initial step of data assessment that primarily addresses issues of completeness and data handling integrity. In data review, the reviewer will ensure that the necessary reporting components have been included in laboratory reports, such as necessary fields (e.g., collection/analysis dates and units) as well as the presence of (but not implications of) QA/QC data components (e.g., LCS records).

The Project laboratory is responsible for reviewing 100% of the analytical data to ensure that it meets the requirements specified by each method. The laboratory system for ensuring valid data includes reviews of the instrument printouts, sample preparation information, calibration information, MS/MSD results, LCS results, method/instrument blanks, and laboratory duplicate results. Data review is performed to assess whether there are nonconformances with the analytical method protocols or Project-specific requirements, and to correct problems discovered.

The laboratory analyst performing the tests shall review 100% of the definitive data. After the analyst's review has been completed, 100% of the data shall be reviewed independently by a senior analyst or by a supervisor. The laboratory QA/QC Manager shall perform a 100% review of 10% of the completed data packages, and the laboratory PM shall perform a review check on all the completed data packages.

3.6 Laboratory Analytical Report

The laboratory analytical report is a standalone report that is provided for each Project task code. The laboratory analytical report typically includes the following data and summary forms:

- detailed case narrative description;
- cross-reference of field sample identifications and laboratory identifications;
- sample results and method reference;
- dates sampled and analyzed;
- COC forms, including air-bill numbers or a copy of the bill of lading;
- documentation of the sample condition upon receipt (as a separate form or on the COC), including cooler temperature;
- a typed report of QA/QC results and acceptance limits that include:
  - method blanks
  - precision (laboratory duplicates)
  - accuracy (MS/MSD, LCS, blank spikes, second source standard checks)
  - initial calibration and continuing calibration summary report;
  - detection/reporting limits;
  - approval signature from a responsible officer of the laboratory; and
  - name and identification of the laboratory, including the state license number.

All samples within a given task code will be batched together and reported in the same laboratory report.

3.7 Corrective Action

The laboratory is required to comply with their SOPs and QAM, which are provided in Appendix C and D. The Laboratory PM will be responsible for ensuring appropriate corrective actions are initiated as required for compliance with this QAPP. All laboratory personnel will be responsible for reporting problems that may compromise the quality of the data.

Laboratory deviations from stated guidelines must be addressed through corrective action. Deviations caused by factors outside the laboratory's control, such as matrix interference, will be noted with an explanation in the report narrative. Calculations will be checked and reports reviewed for errors, oversights, or omissions. The hard copy and electronic laboratory reports for samples and analyses will contain the information necessary to perform data evaluation. The Laboratory PM will follow the

appropriate reporting requirements as written in the laboratory scope of work and associated subcontract.

If QC results exceed the laboratory control limits, the analyst will identify and correct the anomaly before continuing with the sample analyses, if possible. If the QC outlier cannot be overcome with standard corrective action (e.g., re-preparation and/or re-analysis), the Laboratory PM will discuss the causes of the exceedance and steps taken to overcome them in the data package narrative provided. If the exceedance(s) are gross or widespread, Foth will be notified immediately, and the appropriate corrective action will be decided.

After data entry or data transfer procedures from analytical laboratory to Foth are completed for each sample event, data will be inspected for data transcription errors, and corrected as appropriate. After the final QA checks for errors are completed, the data will be added to the Project database.

4. Data Assessment and Usability

SOPs Referenced

- SOP 3113 – Data Verification, Validation, and Qualification

This section describes the stages of data quality assessment that will be used to assess Project data quality and usability.

4.1 Data Quality Metrics

The data generated will be evaluated with respect to precision, accuracy, representativeness, comparability, completeness, and sensitivity. Data Quality Metrics are provided in Table 4-1. Each of these QC indicators is discussed in more detail in the following sections.

4.1.1 Precision

Precision is a measure of the reproducibility of individual measurements and can be assessed through analysis of field or laboratory duplicates. Precision is expressed as the RPD between duplicate analyses, and as percentage of relative standard deviation when more than two analyses are performed on the same sample (triplicate). Laboratory duplicate analyses, such as MS/MSD, LCS/LCSD, and laboratory replicate samples, are also used to assess precision. Precision measurement can be negatively impacted when concentrations approach the MDL. The criteria for precision control limits vary by media and by parameter. Precision is evaluated using the RPD equation:

$$\text{RPD} = \frac{(A - B)}{A + B/2} \times 100$$

Where:
A = Analytical result from one of two duplicate measurements
B = Analytical result from the second measurement

Results will be qualified if the RPD exceeds the applicable QC limit for laboratory duplicates, and/or if the RPD exceeds +/- 20% for field duplicate samples. Precision measurements can be affected by how close a chemical concentration is to the RL, which can increase the percent error (or RPD). At concentrations up to 5x the RL, the absolute difference between the sample and the duplicate will be qualified if it is greater than the RL.

4.1.2 Accuracy

Accuracy is an expression of the degree to which a measured value represents the true value. Accuracy can be assessed in evaluation of the MS, LCS, and ongoing precision and accuracy throughout sample analyses. The criteria and acceptance control limits for accuracy vary by analyte. Accuracy can be expressed via the following equation:

$$\text{Percent Recovery} = \frac{\text{spiked sample result} - \text{unspiked sample result}}{\text{amount of spike added}} \times 100$$

4.1.3 Representativeness

The representativeness expresses the degree to which data accurately and precisely represent the environment and conditions that the sample targeted. Assuming the Project DQOs were upheld in sampling approach and data collection, the samples collected should be considered representative of the environmental conditions they aim to characterize.

4.1.4 Comparability

Comparability expresses the confidence with which one data set can be evaluated in relation to another data set. The extent to which data sets are comparable depends on the similarity of sampling methods and analytical methods. Comparability is satisfied by following sample plans and use of consistent sampling techniques and analytical methods.

4.1.5 Completeness

Completeness measures the amount of data determined to be valid relative to the amount of data that was collected, and can be calculated using the following formula:

$$\text{Completeness (percent)} = \frac{\textit{Number of acceptable data points}}{\textit{Total number data points collected}} \text{ X } 100$$

Completeness is also a measure of the amount of valid data generated versus the amount of data planned for collection, ensuring sufficient data are available to make Project decisions. Field and analytical data completeness goals for this Project are 90% or greater.

4.1.6 Sensitivity

Sensitivity measures:

1) the ability of the analytical method to detect an analyte; and
2) the concentration of the analyte that can reliably be quantified.

The minimum concentration of an analyte that can be detected is the MDL. The minimum concentration that can reliably be quantified is the RL. The MDL and RL will be used as measures of sensitivity for each analysis, as provided in Table 3-1 and Table 3-2 for groundwater and surface water.

The MDL is defined as the lowest concentration of an analyte that can be detected in either a sample or blank with 99% confidence.

RLs are equal to or greater than the lower calibration limit defined by the lowest concentration on the calibration curve. RL are adjusted for each sample based on the amount of sample extracted, dilution factors, and percent moisture (for solid samples). All laboratories will report detected concentrations above the RL as may be applicable without qualification and report detected concentrations between the MDL and RL with a J-qualifier to indicate that the concentration is an estimated value.

4.2 Data Usability

Analytical data will be subjected to review (SOP – 3113 Data Verification, Validation, and Qualification) to assess for bias and to review for data usability. Data usability is comprised of completeness, representativeness, and applicable levels of precision and accuracy. One hundred percent of the data will undergo data verification by Foth.

The USEPA CLP National Functional Guidelines for Inorganic Data Review EPA National Functional Guidelines for Inorganic Data Review (USEPA, 2017a) and EPA National Functional Guidelines for Organic Data Review (USEPA, 2017b) will be used as guidance for the data review. The functional guidelines provide general data verification and validation guidelines that can be applied to data generated for the baseline studies.

Data qualifiers (i.e., flags) will be applied to those analytical results that fall outside of the DQO tolerance limits established for the Project or the applicable method criteria. The data quality calculations in Table 4-2 are the basis for assigning data qualifiers. Results of the data review will be documented, archived in the Project file, and summarized in the applicable technical memoranda.

The laboratory data will be reviewed for compliance with the applicable method and the quality of the data reported. The following summarizes the areas of data verification and data validation:

- data completeness;
- holding times;
- blanks;
- laboratory control samples;
- MS/MSDs;
- LCS; and
- field duplicates.

The application of data validation criteria is a function of project-specific DQOs. The Project QA/QC manager will evaluate if the DQOs have been met.

4.3 Data Verification and Data Validation

Data verification and validation is a more technical process than data review in that the core technical aspects of data quality (e.g., precision and accuracy) are evaluated through a review of the results of QA/QC measures, such as LCS. Data verification and validation will proceed per guidance and procedures outlined within the following documents:

- QC limits specified in this QAPP.
- Method-specific and laboratory-established QC requirements, as applicable.
- Guidance on Environmental Data Verification and Validation (USEPA, 2002).
- Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use. OSWER No. 9200.1-85. EPA 540-R-08-005 (USEPA, 2009).
- National Functional Guidelines for Inorganic Superfund Methods Data Review (USEPA, 2017a).
- National Functional Guidelines for Organic Data Review (USEPA, 2017b).

All analytical data (100%) will undergo Stage 2A data validation (USEPA, 2002). The following will be reviewed, as applicable to the analysis:

- Case narrative discussing any applicable analytical problems and procedures
- COC forms and sample receipt condition
- Holding times
- Method blanks
- MS/MSD recoveries and RPD values
- LCS/LCSD recoveries and RPD values
- Field duplicate sample RPD values
- Laboratory duplicate RPD values
- Detection and reporting limits

- Equipment blanks

4.3.1 Data Verification and Validation Summary Report

A data verification and validation summary technical memorandum will be provided for each sampling event, and will include the following sections:

- Introduction
- Data Quality Assessment and Data Qualifiers
- Sample Preservation and Temperature Upon Laboratory Receipt
- Holding Times
- Method Blank Contamination
- LCS/LCS Duplicate Recovery and RPD
- MS/MSD Recovery and RPD
- Field QC Samples
- Completeness Summary
- Conclusion

The technical memorandum will be placed in the Project file and a copy given to the client.

4.3.2 Data Qualifiers

The results of the data quality review, including text assigning qualifiers in accordance with the USEPA National Functional Guidelines (USEPA, 2017a and USEPA, 2017b) and a tabular summary of qualifiers, will be generated by the data validator and documented within the data verification and validation technical memorandum. Data qualifiers will be applied to specific sample results when there are nonconformances that could potentially affect data usability.

4.4 Data Management

A data management process will be used to track, review, analyze, report, and file Project data. Project data will include technical and non-technical information in hard copy and electronic formats. The types of data will include primary data and metadata. The primary data will be subject data, metadata will be information about the primary data. In general, the data flow process will include the following:

- field data acquisition with electronic or manual (e.g., field book) transcription;
- download, review, and digitize field data to spreadsheets, analyze and reduce for reporting;
- receive analytical data from laboratory, analyze, reduce for reporting, and format for uploading to EQuIS database (.txt, .xls, or other common format that EQuIS will import);
- import file to EQuIS database and check values relative to original laboratory report (original laboratory reports are stored on server in pdf format, and hard copy of reports are stored in the Master File);
- perform data reduction and validation work to generate approved data sets and electronic files;
- save and store original and approved data sets and electronic files on Foth server Project file directory; and
- route original files to Project file on ProjectWise for storage.

The field and analytical data will be managed in the EQuIS database by Foth. Data management protocols for both field data and electronic data will be implemented to provide consistent, accurate, and defensible documentation of data quality; these protocols are described in more detail in Section 5. Electronic field and laboratory data will be incorporated into the Project database. Internal management of electronic data files will be performed using EQuIS. Sampling and monitoring data will be submitted in standard Foth EDD format.

5. Project Quality Assurance

This section summarizes the primary QA documents and activities which will be used to formalize and track quality related to Project activities.

5.1 Quality Assurance Project Plan

The QAPP is a living document that will be regularly updated as the Project evolves. Its function at the beginning of the Project is essential because it sets up the activities, methods, measures, and standards that are planned to obtain quality Project data and reports. During the Project, it is an important reference document that states measures and processes to be used to evaluate quality.

5.2 Quality Assurance/Quality Control Assessments and Reviews

This section addresses performance and system audits, QA milestones, corrective actions, and the management of QA records. All members of the Project team are encouraged to communicate quality concerns openly within the Project team.

QA/QC assessments and reviews are performed within the scope of data collection planning, sampling and data collection, data reduction and modeling, and reporting. Personnel responsible for providing QA/QC assessments are task dependent, but the QA Officer leads the process. System and performance audits are also led by the Technical Lead and Chemistry QA Manager, or a suitable designee for the relevant task. Quality assessment requires reporting of QA/QC milestones, corrective actions needed to maintain quality, and the generation and upkeep of the QA record for the Project.

5.2.1 System Audits

A system audit determines that each element within an activity is functioning appropriately and is within the guidelines specified by this QAPP. These types of audits will be conducted on field sampling, preservation, shipping, and equipment calibration/cleaning procedures by the Technical Lead. These audits may be conducted during the life of this Project. A systems audit will include a review of the sampling/analysis plan, sample collection/measurement methods, sampling protocol, field COC procedures, field documentation methods, and sample identification methods. If this audit is conducted, the audit will be finalized as a memorandum and will be placed in the Project file, with a copy given to the PM and to the client.

5.2.2 Performance Audits

These types of audits may be conducted on field or laboratory activities. Foth reserves the right to audit laboratories used for analyses on a regular basis or if there are inappropriate trends in the laboratory data, major changes in personnel, and/or discrepancies in QC samples. These audits will be conducted at the request of and under the supervision of the Chemistry QA Manager. If this audit is conducted, it will be finalized as a memorandum and placed in the Project file with a copy given to the PM and to the client.

5.3 Quality Assurance/Quality Control Milestones

QA/QC milestones for this Project are during and within two weeks following field sampling and other major field events, after the reduction of major laboratory data sets, after the generation of reports and major technical memoranda, and upon the completion of system and performance audits. The timing of corrective actions and controls and the QA record will be organized according to the major Project activities.

5.4 Quality Assurance/Quality Control Corrective Action and Controls

The QAPP and associated documentation includes QC measures to resolve detected quality problems or issues that may be identified during the Project. In addition, the QA Officer will take steps under his or her discretion, with approval of the PM, for corrective action and controls. All significant corrective actions and control measures will be documented in the QA record.

A nonconformance is any procedure, event, reading, or measurement which is outside the limits established for field operations.

As a result of a nonconformance, whether identified by the Technical Lead, Chemistry QA Manager, the sampling technician, or by an auditor, a corrective action shall be implemented. Any one of the individuals indicated above can initiate a corrective action, if necessary.

Corrective actions are generally of two kinds:

- Immediate, to recalibrate or repair nonconforming equipment. The need for such an action will most frequently be identified by the field technician.

- Long-term, to eliminate causes of nonconformance and to minimize the possibility of their recurrence. These are usually system-related issues that may be identified as the result of QC reports associated with one or more projects.

The result of any equipment/instrument readings depends on the inherent accuracy and proper operation, use, and function of the instrument. It is essential that the equipment/instruments operate under optimum conditions at all times. Each equipment/instrument user is expected to be familiar with the manufacturer's operations manual on each instrument and routinely performs various service checks.

Routine field preventive maintenance procedures are found in Table 5-1. Routine laboratory preventive maintenance procedures are provided in Eurofins QAM Wand, the laboratory analytical SOPs, which are provided in Appendices C and D.

Depending on the nature of a problem, a corrective action employed may be formal or informal. An informal corrective action consists of an evaluation of a nonconforming situation that threatens the outcome of a procedure, event, reading, or measurement. Upon recognition of the problem, the following steps will be taken.

1. Attempts made by field technician to correct the problem immediately, by referencing available service information. Samples are returned to proper storage during troubleshooting.

2. The Technical Lead is appraised that an equipment malfunction is disrupting normal field sampling activities. Attempts made to correct failure are described.

3. The Technical Lead decides whether to involve outside servicing. This decision is based on the nature of the problem and availability of service assistance and parts.

4. The PM is informed and an assessment of the time required to restore proper equipment function in relation to remaining sample-holding time is made.

5. The Technical Lead selects an approved alternate analytical method, if possible, which will permit completion of field activities within applicable time limits (if any).

6. The field technician or Technical Lead arranges with another equipment source to complete the field measurements within remaining holding time and by approved methodology.

7. The field technician will review their procedure for apparent errors, recalibrate the instrument used for measurement, and re-measure.

If this does not result in correction of the problem, the field technician will bring the problem to the attention of the appropriate manager who will determine the proper corrective action. If significant time or costs are involved, the manager will obtain the necessary approval for the corrective action indicated. The corrective action will be incorporated into the appropriate procedures to minimize the possibility of recurrence.

In either case, occurrence of the problem; corrective action taken; and verification of problem resolution must be documented. Documentation of corrective action will be made in the field log book.

Laboratory corrective actions are summarized in Eurofins QAMs (Appendix C).

5.5 Quality Assurance/Quality Control Records

Each equipment/instrument is calibrated according to the manufacturer's instructions. A maintenance log will be maintained for each instrument. This maintenance log will include the following (at a minimum):

- Instrument description.
- Manufacturer, model number, and serial number.
- Name, address, and telephone number of company which services item.
- Type of service policy.
- Timing and frequency of routine maintenance, servicing, and calibration.

Records shall be maintained to provide evidence of QA activities. All activities which indicate an out-of-control situation will be evaluated. Corrective action taken will be documented. This documentation will be in the Project log book (field records) or in formal memorandums, letters, or notifications which are part of the Project file.

6. Reporting

The focus of this QAPP is the environmental baseline data collection of surface water and groundwater. Reporting of those data will be accomplished in the form of memoranda. Each sampling event generates data including field data and observations as well as carefully collected water samples to be processed at a laboratory. The QAPP addresses collection, processing, and analyzing laboratory associated data and describes data validation and quality management of those data in preceding sections. Memoranda scope and description are provided in this section. Additionally, there may be reports generated that contain further analysis, evaluation, trending, statistics, and comparisons.

6.1 Memoranda Preparation for Quarterly Sampling Events

A memorandum will be used to summarize sampling activities or single occurrence activities. The scope of the technical memorandum is to communicate the results of the sampling event. Analysis and interpretations is not included in this deliverable. A technical memorandum may include the following:

- summary of the monitoring program;
- field measurement and sampling methodology;
- field results and data analysis;
- data interpretation;
- summary tables with sample locations, water quality analytical results compared to applicable standards, hydrologic information, and QA/QC data review;
- summary of stream flow calculations.
- attachments including field monitoring forms, calibration documents, and photographic logs of groundwater and surface water monitoring locations.

6.2 Analysis Summary Report

An analysis summary report may be prepared to provide a comprehensive perspective of a series of monitoring activities. The purpose of the summary report is to analyze and summarize hydrologic and/or analytical trends and provide recommendations for expansion or optimization of the monitoring network. A summary report may include the following:

- summary of monitoring activities for the year or determined time frame;
- list of locations that were sampled, including sample dates and analyses performed;
- table of field measurements;
- table of detected target constituents for each monitoring location;
- hydrographs for each of the monitoring locations;
- maps showing hydrologic and/or analytical contours;
- trend graphs of hydrologic and/or analytical data;
- copies of laboratory reports and data verification summaries;
- data review summary report; and
- recommendations for expansion or revisions to the monitoring plan, as appropriate.

For reference, the summary report may also share data and modeling results from other studies near the Project site.

7. References

Foth Infrastructure & Environment, LLC, 2024a. Groundwater Characterization and Monitoring Work Plan. May 2024.

Foth Infrastructure & Environment, LLC, 2024b. Surface Water Monitoring Work Plan. May 2024.

United States Environmental Protection Agency, 2002. Guidance on Environmental Data Verification and Data Validation. https://www.epa.gov/sites/default/files/2015-06/documents/g8-final.pdf

United States Environmental Protection Agency, 2009. Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use. https://nepis.epa.gov/Exe/ZyPDF.cgi/P1002WWF.PDF?Dockey=P1002WWF.PDF

United States Environmental Protection Agency, 2017a. EPA National Functional Guidelines for Inorganic Data Review. https://www.epa.gov/sites/default/files/2017-01/documents/national_functional_guidelines_for_inorganic_superfund_methods_data_review_01302017.pdf

United States Environmental Protection Agency, 2017b. EPA National Functional Guidelines for Organic Data Review. https://www.epa.gov/sites/default/files/2017-01/documents/national_functional_guidelines_for_organic_superfund_methods_data_review_013072017.pdf

Tables

Table 2-1
Groundwater Monitoring - Sample Containers, Preservatives, and Hold Times

Analyte	Method (from Work Plan)	EuroFins Method	Container	Sample Volume	Preservation	Hold Time
General Parameters						
Ammonia (un-ionized as N)	350.1	350.1	Plastic	250 mL	0-6°C	NA
Alkalinity, Total	2320B	2320B	Plastic	250 mL	0-6°C	14 days
Alkalinity, Bicarbonate as CaCO3	2320B	2320B	Plastic	250 mL	0-6°C	14 days
Bromide	4500	300_28D	Plastic	500 mL	0-6°C	28 days
Chloride	4500	300_28D	Plastic	500 mL	0-6°C	28 days
Cyanide, free	USEPA 335.4	335.4	Plastic	250 mL	Sodium Hydroxide, 0-6°C	
Dissolved Organic Carbon	5310	5310	2x VOA vials	40mL (x2)	Sulfuric acid, 0-6°C	28 days
Total Organic Carbon	5310C	5310	2x VOA vials	40mL (x2)	Sulfuric acid, 0-6°C	28 days
Fluoride	4500	300_28D	Plastic	500 mL	0-6°C	28 days
Hardness (Ca+Mg)	2340B	2340B	Plastic	250 mL	nitric acid	180 days
Nitrate (as NO3-N)	300.0	300.0	Plastic	500 mL	0-6°C	48 hours
Nitrate (as N)	4500	300_48Hr	Plastic	500 mL	0-6°C	48 hours
Nitrite (as N)	4500	300_48Hr	Plastic	500 mL	0-6°C	48 hours
Nitrate + Nitrite (as N)	4500	300_48Hr	Plastic	500 mL	0-6°C	48 hours
Phosphorus, total	4500	365.1	Plastic	500 mL	Sulfuric acid, 0-6°C	28 days
Sulfate	300.0	300_28D	Plastic	500 mL	0-6°C	28 days
Sulfide	4500	SM4500_S2_F	Plastic	500 mL	Zn acetate & NaOH	7 days
Total Dissolved Solids (TDS)	2540C	2540C	Plastic	500 mL	0-6°C	7 days
Total Salinity	2520	2520B	Plastic	250 mL	0-6°C	NA
Total Suspended Solids (TSS)	2540D	2540D	Plastic	1 L	0-6°C	7 days
Metals (Total & Dissolved)						
Aluminum	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Antimony	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Arsenic	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Barium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Beryllium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Boron	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Cadmium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Calcium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Chromium (total)	200.8	6020B	Plastic	250 mL	Nitric acid	180 days
Chromium +3	200.8	3500_CR+3_B	calculation	NA	NA	NA
~~Chromium +6~~	~~200.8~~	~~3500_CR_B~~	~~Plastic~~	~~500 mL~~	~~0-6°C~~	~~24 Hours~~
Cobalt	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Copper	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Iron	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Lead	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Lithium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Manganese	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Magnesium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Mercury, Low Level	1631E	1631E	LLHg kit, 2x VOA vials	40mL (x2)	0-6°C	28 days
Methyl Mercury	1630	1630ME	Glass	250 ml	HCL	
Molybdenum	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Nickel	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Potassium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Selenium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Silver	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Sodium	6020A	6020B	Plastic	250 mL	Nitric acid	180 days
Strontium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Thallium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Tin	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Uranium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Vanadium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Zinc	6020	6020B	Plastic	250 mL	Nitric acid	180 days

Notes:
°C = degrees Celsius
mL = milliliter
NA = Not Applicable

Prepared by: NMG1
Checked by: NB (Eurofins)

Table 2-2
Groundwater Quality Stabilization Parameters

Parameter	Range	Limits
Dissolved Oxygen	+/- 0.5 mg/L	+/- 10%
Specific Conductance	+/- 5.0 µmhos/cm for values <1,000 µmhos/cm +/- 10.0 µmhos/cm for values > 1,000 umhos/cm	+/- 3% +/- 3%
pH	+/- 0.1 pH standard units	+/- 0.1 pH standard nits
Temperature	+/- 0.1 ºC	+/- 3%
Turbidity	< 5 NTUs (Required if metals samples will not be filtered. Recommended if sorptive compounds or elements are collected. Optional, but recommended if other compounds or elements are collected.	+/- 10% (for values greater than 1 NTU)
Oxidation Reduction Potential	+/- 10 mv	--
Water Level	No change in water level	--

Notes:

ºC = degrees Celsius

mg/L = milligrams per liter

mv = millivolts

NTU = Nephelometric Turbidity Unit

µmhos/cm = micromhos per centimeter

Prepared by: MCC2

Checked by: NMG1

Table 2-3
Surface Water Monitoring - Sample Containers, Preservatives, and Hold Times

Analyte	Method (from Work Plan)	Method	Container	Sample Volume	Preservation	Hold Time
General Parameters						
Ammonia (un-ionized as N)	350.1	350.1	Plastic	250 mL	0-6°C	NA
Alkalinity, Total	2320B	2320B	Plastic	250 mL	0-6°C	14 days
Alkalinity, Bicarbonate as CaCO3	2320B	2320B	Plastic	250 mL	0-6°C	14 days
Bromide	4500	300_28D	Plastic	500 mL	0-6°C	28 days
Chloride	4500	300_28D	Plastic	500 mL	0-6°C	28 days
Cyanide, free	USEPA 335.4					
Dissolved Organic Carbon	5310	5310	2x VOA vials	40mL (x2)	Sulfuric acid, 0-6°C	28 days
Total Organic Carbon	5310C	5310	2x VOA vials	40mL (x2)	Sulfuric acid, 0-6°C	28 days
Fluoride	4500	300_28D	Plastic	500 mL	0-6°C	28 days
Hardness (Ca+Mg)	2340B	6020B	Plastic	250 mL	nitric acid	180 days
Nitrate (as NO3-N)	300.0	300_48Hr	Plastic	500 mL	0-6°C	48 hours
Nitrate (as N)	4500	300_48Hr	Plastic	500 mL	0-6°C	48 hours
Nitrite (as N)	4500	300_48Hr	Plastic	500 mL	0-6°C	48 hours
Nitrate + Nitrite (as N)	4500	300_48Hr	Plastic	500 mL	0-6°C	48 hours
Phosphorus, total	4500	4500_P_E	Plastic	500 mL	Sulfuric acid, 0-6°C	28 days
Sulfate	300.0	300_28D	Plastic	500 mL	0-6°C	28 days
Sulfide	4500	SM4500_S2_F	Plastic	500 mL	Zn acetate & NaOH	7 days
Total Dissolved Solids (TDS)	2540C	2540D	Plastic	500 mL	0-6°C	7 days
Total Salinity	2520	2520B	Plastic	250 mL	0-6°C	NA
Total Suspended Solids (TSS)	2540D	2540D	Plastic	1 L	0-6°C	7 days
Metals (Total & Dissolved)						
Aluminum	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Antimony	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Arsenic	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Barium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Beryllium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Boron	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Cadmium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Calcium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Chromium (total)	200.8	6020B	Plastic	250 mL	Nitric acid	180 days
Chromium +3	200.8	3500_CR+3_B	calculation	NA	NA	NA
~~Chromium +6~~	~~200.8~~	~~3500_CR_B~~	~~Plastic~~	~~500 mL~~	~~0-6°C~~	~~24 Hours~~
Cobalt	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Copper	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Iron	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Lead	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Lithium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Manganese	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Magnesium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Mercury, Low Level	1631E	1631E	LLHg kit, 2x VOA vials	40mL (x2)	0-6°C	28 days
Methyl Mercury	1630					
Molybdenum	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Nickel	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Potassium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Selenium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Silver	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Sodium	6020A	6020B	Plastic	250 mL	Nitric acid	180 days
Strontium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Thallium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Tin	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Uranium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Vanadium	6020	6020B	Plastic	250 mL	Nitric acid	180 days
Zinc	6020	6020B	Plastic	250 mL	Nitric acid	180 days

Notes:
°C = degrees Celsius
mL = milliliter
NA = Not Applicable

Prepared by: NMG1
Checked by: NB (Eurofins)

Table 3-1
Groundwater Monitoring Analytical Parameters

Analyte	CAS-RN	Laboratory	Method	Method Detection Limit	Reporting Limit	Units	MS/MSD Control Limits	RPD	LCS Control Limits	RPD
General Parameters										
Ammonia (un-ionized as N)	7664-41-7	Eurofins	350.1	0.1	0.2	mg/L	NA	NA	NA	NA
Alkalinity, Total	STL00171	Eurofins	2320B	3.74	5	mg/L	NA	NA	95-121	20
Alkalinity, Bicarbonate as CaCO3	STL00138	Eurofins	2320B	3.74	5	mg/L	NA	NA	NA	NA
Bromide	24959-67-9	Eurofins	300.0_28D	0.179	1	mg/L	80-120	20	90-110	20
Chloride	16887-00-6	Eurofins	300.0_28D	0.116	1	mg/L	80-120	20	90-110	20
Cyanide, free	STL00131	Eurofins	335.4	NA	NA	NA	NA	NA	NA	NA
Dissolved Organic Carbon	7440-44-0	Eurofins	SM5310_DOC_C	0.47	1	mg/L	75-125	20	86-116	20
Total Organic Carbon		Eurofins								
Fluoride	16984-48-8	Eurofins	300.0_28D	0.191	1	mg/L	80-120	20	90-110	20
Hardness (Ca+Mg)	STL00009	Eurofins	SM2340B	0.455	0.91	mg/L				
Nitrate (as NO3-N)		Eurofins								
Nitrate (as N)	14797-55-8	Eurofins	300_48HR	0.043	1	mg/L	80-120	20	90-110	20
Nitrite (as N)	14797-65-0	Eurofins	300_48HR	0.07	1	mg/L	80-120	20	90-110	20
Nitrate + Nitrite (as N)	STL00217	Eurofins	300_48HR	0.07	1	mg/L	NA	NA	NA	NA
Phosphorus, total	7723-14-0	Eurofins	365.1	0.239	0.05	mg/L	75-125	20	88-123	20
Sulfate	14808-79-8	Eurofins	300.0_28D	0.207	1	mg/L	80-120	20	90-110	20
Sulfide	18496-25-8	Eurofins	SM4500_S2_F	0.231	1	mg/L	75-125	20	85-115	20
Total Dissolved Solids (TDS)	STL00242	Eurofins	2540C	4.34	10	mg/L	75-125	20	80-120	20
Total Salinity	STL00226	Eurofins	SM2520_B	0.33	0.33	psu	NA	NA	NA	NA
Total Suspended Solids (TSS)	STL00161	Eurofins	2540D	1.93	5	mg/L	75-125	20	80-120	20
Metals (Total & Dissolved)										
Aluminum	7429-90-5	Eurofins	6020B	24.6	100	µg/L	75-125	20	80-120	20
Antimony	7440-36-0	Eurofins	6020B	1.32	3	µg/L	75-125	20	80-120	20
Arsenic	7440-38-2	Eurofins	6020B	0.232	1	µg/L	75-125	20	80-120	20
Barium	7440-39-3	Eurofins	6020B	0.73	2.5	µg/L	75-125	20	80-120	20
Beryllium	7440-41-7	Eurofins	6020B	0.53	1	µg/L	75-125	20	80-120	20
Boron	7440-42-8	Eurofins	6020B	12.7	50	µg/L	75-125	20	80-120	20
Cadmium	7440-43-9	Eurofins	6020B	0.167	0.5	µg/L	75-125	20	80-120	20
Calcium	7440-70-2	Eurofins	SM2340B	0.1	0.2	mg/L	NA	NA	NA	NA
Chromium (total)	7440-47-3	Eurofins	6020B	1.14	5	µg/L	75-125	20	80-120	20
Chromium +3	16065-83-1	Eurofins	3500_CR3_B	0.01	0.01	mg/L	NA	NA	NA	NA
~~Chromium +6~~	~~18540-29-9~~	~~Eurofins~~	~~3500_CR_B~~	~~0.00319~~	~~0.01~~	~~mg/L~~	~~85-115~~	~~20~~	~~85-115~~	~~20~~
Cobalt	7440-48-4	Eurofins	6020B	0.402	1	µg/L	75-125	20	80-120	20
Copper	7440-50-8	Eurofins	6020B	0.497	2	µg/L	75-125	20	80-120	20
Iron	7439-89-6	Eurofins	6020B	46.7	100	µg/L	75-125	20	80-120	20
Lead	7439-92-1	Eurofins	6020B	0.186	0.5	µg/L	75-125	20	80-120	20
Lithium	7439-93-2	Eurofins	6020B	2.5	10	µg/L	75-125	20	80-120	20
Manganese	7439-96-5	Eurofins	6020B	0.791	2.5	µg/L	75-125	20	80-120	20
Magnesium	7439-95-4	Eurofins	6020B	49.4	200	µg/L	75-125	20	80-120	20
Mercury, Low Level	7439-97-6	Eurofins	1631E	0.2	0.5	ng/L	71-125	24	77-123	24
Methyl Mercury	22967-92-6	Eurofins	1630_ME	0.2	0.5	ng/L	65-135	35	65-135	35
Molybdenum	7439-98-7	Eurofins	6020B	2.46	5	µg/L	75-125	20	80-120	20
Nickel	7440-02-0	Eurofins	6020B	0.625	2	µg/L	75-125	20	80-120	20
Potassium	7440-09-7	Eurofins	6020B	111	500	µg/L	75-125	20	80-120	20
Selenium	7782-49-2	Eurofins	6020B	0.982	2.5	µg/L	75-125	20	80-120	20
Silver	7440-22-4	Eurofins	6020B	0.115	0.5	µg/L	75-125	20	80-120	20
Sodium	7440-23-5	Eurofins	6020B	77.3	200	µg/L	75-125	20	80-120	20
Strontium	7440-24-6	Eurofins	6020B	0.637	4	µg/L	75-125	20	80-120	20
Thallium	7440-28-0	Eurofins	6020B	0.57	2	µg/L	75-125	20	80-120	20
Tin	7440-31-5	Eurofins	6020B	1.3	5	µg/L	75-125	20	80-120	20
Uranium	7440-61-1	Eurofins	1638	0.0098	0.03	µg/L	70-130	20	85-115	20
Vanadium	7440-62-2	Eurofins	6020B	2.15	5	µg/L	75-125	20	80-120	20
Zinc	7440-66-6	Eurofins	6020B	6.92	20	µg/L	75-125	20	80-120	20

Notes:
LCS = laboratory control samples
mg/L = milligrams per liter
MS/MSD = matrix spike/matrix spike duplicate
NA = Not Applicable
RPD = relative percent difference
µg/L = microgram per liter

Prepared by: NMG1
Checked by: NB (Eurofins)

Table 3-2
Surface Water Monitoring Analytical Parameters

Analyte	CAS-RN	Laboratory	Method	Method Detection Limit	Reporting Limit	Units	MS/MSD Control Limits	RPD	LCS Control Limits	RPD
General Parameters										
Ammonia (un-ionized as N)	7664-41-7	Eurofins	350.1	0.1	0.2	mg/L	NA	NA	NA	NA
Alkalinity, Total	STL00171	Eurofins	2320B	3.74	5	mg/L	NA	NA	95-121	20
Alkalinity, Bicarbonate as CaCO3	STL00138	Eurofins	2320B	3.74	5	mg/L	NA	NA	NA	NA
Bromide	24959-67-9	Eurofins	300.0_28D	0.179	1	mg/L	80-120	20	90-110	20
Chloride	16887-00-6	Eurofins	300.0_28D	0.116	1	mg/L	80-120	20	90-110	20
Cyanide, free	STL00131	Eurofins	335.4	NA	NA	NA	NA	NA	NA	NA
Dissolved Organic Carbon	7440-44-0	Eurofins	SM5310_DOC_C	0.47	1	mg/L	75-125	20	86-116	20
Total Organic Carbon		Eurofins								
Fluoride	16984-48-8	Eurofins	300.0_28D	0.191	1	mg/L	80-120	20	90-110	20
Hardness (Ca+Mg)	STL00009	Eurofins	SM2340B	0.455	0.91	mg/L				
Nitrate (as NO3-N)		Eurofins								
Nitrate (as N)	14797-55-8	Eurofins	300_48HR	0.043	1	mg/L	80-120	20	90-110	20
Nitrite (as N)	14797-65-0	Eurofins	300_48HR	0.07	1	mg/L	80-120	20	90-110	20
Nitrate + Nitrite (as N)	STL00217	Eurofins	300_48HR	0.07	1	mg/L	NA	NA	NA	NA
Phosphorus, total	7723-14-0	Eurofins	365.1	0.239	0.05	mg/L	75-125	20	88-123	20
Sulfate	14808-79-8	Eurofins	300.0_28D	0.207	1	mg/L	80-120	20	90-110	20
Sulfide	18496-25-8	Eurofins	SM4500_S2_F	0.231	1	mg/L	75-125	20	85-115	20
Total Dissolved Solids (TDS)	STL00242	Eurofins	2540C	4.34	10	mg/L	75-125	20	80-120	20
Total Salinity	STL00226	Eurofins	SM2520_B	0.33	0.33	psu	NA	NA	NA	NA
Total Suspended Solids (TSS)	STL00161	Eurofins	2540D	1.93	5	mg/L	75-125	20	80-120	20
Metals (Total & Dissolved)										
Aluminum	7429-90-5	Eurofins	6020B	24.6	100	µg/L	75-125	20	80-120	20
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Barium	7440-39-3	Eurofins	6020B	0.73	2.5	µg/L	75-125	20	80-120	20
Beryllium	7440-41-7	Eurofins	6020B	0.53	1	µg/L	75-125	20	80-120	20
Boron	7440-42-8	Eurofins	6020B	12.7	50	µg/L	75-125	20	80-120	20
Cadmium	7440-43-9	Eurofins	6020B	0.167	0.5	µg/L	75-125	20	80-120	20
Calcium	7440-70-2	Eurofins	SM2340B	0.1	0.2	mg/L	NA	NA	NA	NA
Chromium (total)	7440-47-3	Eurofins	6020B	1.14	5	µg/L	75-125	20	80-120	20
Chromium +3	16065-83-1	Eurofins	3500_CR3_B	0.01	0.01	mg/L	NA	NA	NA	NA
~~Chromium +6~~	~~18540-29-9~~	~~Eurofins~~	~~3500_CR_B~~	~~0.00319~~	~~0.01~~	~~mg/L~~	~~85-115~~	~~20~~	~~85-115~~	~~20~~
Cobalt	7440-48-4	Eurofins	6020B	0.402	1	µg/L	75-125	20	80-120	20
Copper	7440-50-8	Eurofins	6020B	0.497	2	µg/L	75-125	20	80-120	20
Iron	7439-89-6	Eurofins	6020B	46.7	100	µg/L	75-125	20	80-120	20
Lead	7439-92-1	Eurofins	6020B	0.186	0.5	µg/L	75-125	20	80-120	20
Lithium	7439-93-2	Eurofins	6020B	2.5	10	µg/L	75-125	20	80-120	20
Manganese	7439-96-5	Eurofins	6020B	0.791	2.5	µg/L	75-125	20	80-120	20
Magnesium	7439-95-4	Eurofins	6020B	49.4	200	µg/L	75-125	20	80-120	20
Mercury, Low Level	7439-97-6	Eurofins	1631E	0.2	0.5	µg/L	71-125	24	77-123	24
Methyl Mercury	22967-92-6	Eurofins	1630_ME	0.2	0.5	µg/L	65-135	35	65-135	35
Molybdenum	7439-98-7	Eurofins	6020B	2.46	5	µg/L	75-125	20	80-120	20
Nickel	7440-02-0	Eurofins	6020B	0.625	2	µg/L	75-125	20	80-120	20
Potassium	7440-09-7	Eurofins	6020B	111	500	µg/L	75-125	20	80-120	20
Selenium	7782-49-2	Eurofins	6020B	0.982	2.5	µg/L	75-125	20	80-120	20
Silver	7440-22-4	Eurofins	6020B	0.115	0.5	µg/L	75-125	20	80-120	20
Sodium	7440-23-5	Eurofins	6020B	77.3	200	µg/L	75-125	20	80-120	20
Strontium	7440-24-6	Eurofins	6020B	0.637	4	µg/L	75-125	20	80-120	20
Thallium	7440-28-0	Eurofins	6020B	0.57	2	µg/L	75-125	20	80-120	20
Tin	7440-31-5	Eurofins	6020B	1.3	5	µg/L	75-125	20	80-120	20
Uranium	7440-61-1	Eurofins	1638	0.0098	0.03	µg/L	70-130	20	85-115	20
Vanadium	7440-62-2	Eurofins	6020B	2.15	5	µg/L	75-125	20	80-120	20
Zinc	7440-66-6	Eurofins	6020B	6.92	20	µg/L	75-125	20	80-120	20

Notes:
LCS = laboratory control samples
mg/L = milligrams per liter
MS/MSD = matrix spike/matrix spike duplicate
NA = Not Applicable
RPD = relative percent difference
µg/L = microgram per liter

Prepared by: NMG1
Checked by: NB (Eurofins)

Table 4-1
Data Quality Metric and Evaluation Criteria

Data Quality Metric	Quality Control Analysis	Applicable Method	Collection Frequency	Evaluation Criteria
Precision	Blind Duplicate	General Chemistry / Metals	5% of primary samples	RPD
	MS/MSD	General Chemistry / Metals	Per analytical batch	RPD
	LCS/LCSD	General Chemistry / Metals	Per analytical batch	RPD
	Laboratory Duplicate	General Chemistry / Metals	Per analytical batch	RPD
Accuracy	MS	General Chemistry / Metals	Per analytical batch	Percent recovery
	LCS	General Chemistry / Metals	Per analytical batch	Percent recovery
Representativeness	Method Blanks	General Chemistry / Metals	Per analytical batch	Qualitative
	Field Blanks	General Chemistry / Metals	Per primary Mercury sample, 5% of primary samples for other analytes	Qualitative
	Equipment Blanks	General Chemistry / Metals	5% of primary samples	Qualitative
	Blind Duplicate	General Chemistry / Metals	5% of primary samples	Qualitative
	Holding Times	General Chemistry / Metals	Applicable to all methods	Qualitative
Comparability	Field Procedures	General Chemistry / Metals	--	Qualitative
	Analytical Methods	General Chemistry / Metals	--	Qualitative
	Units of Measure	General Chemistry / Metals	--	Qualitative
Completeness	Valid Data	General Chemistry / Metals	--	Percent acceptable data
Sensitivity	Reporting Limits	General Chemistry / Metals	--	Qualitative

Notes:

Prepared by: MCC2

Checked by: NMG1

Equipment blanks are not collected if dedicated sampling equipment is used

LCS/LCSD = laboratory control sample/ laboratory control sample duplicate

MS/MSD = matrix spike/matrix spike duplicate

RPD = relative percent difference

Table 4-2

Data Quality Calculations

Statistic	Symbol	Formula	Definition	Uses
Relative Standard Deviation	RSD	$\left(s / \bar{x}\right)$ x 100	Relative standard deviation, adjusts for magnitude of observations	Used to assess precision for replicate results
Percent Difference	%D	$\left(\frac{(x_1 - x_2)}{x_1}\right)$ x 100	Measure of the difference of 2 observations	Used to assess accuracy
Relative Percent Difference	RPD	$\left(\frac{(x_1 - x_2)}{(x_1 + x_2)/2}\right)$ x 100	Measure of variability that adjusts for the magnitude of observations	Used to assess total and analytical precision of duplicate measurements
Percent Recovery	%R	$\frac{\left(\begin{array}{c}\text{value of} \\ \text{spiked} \\ \text{sample}\end{array} - \begin{array}{c}\text{value of} \\ \text{unspiked} \\ \text{sample}\end{array}\right)}{\text{Value of added spike}}$ x 100	Recovery of spiked compound in sample matrix	Used to assess matrix effects and total precision
Percent Completeness	%Complete	$\left(\frac{\text{\# of usable results}}{\text{\# of reported}}\right)$ x 100	Measure of valid, usable data	Used to assess data completeness

Notes:

Prepared by: MCC2
Checked by: NMG1

s = standard deviation

$\bar{x}$ = average analyte concentration

x = observed analyte concentration

= number

Table 5-1
Routine Field Preventive Maintenance Procedures

Instrument	Activity	Frequency
pH Meter	Calibrate per manufacture's instruction	Daily prior to use
	Rinse electrodes with deionized or distilled water	After each reading
	Immerse electrodes if required to do so based on type of electrode	When not in use
	Clean electrodes with mild acid or alcohol solution	When dirty or coated with precipitate
	Check batteries (if any)	Prior to each use
Conductivity Meter	Calibrate per manufacture's instruction	Daily prior to use
	Rinse probe with deionized or distilled water	After each reading
	Check batteries (if any)	Prior to each use
Dissolved Oxygen Meter	Calibrate per manufacture's instruction	Daily prior to use
	Rinse probe with deionized or distilled water	After each reading
	Check batteries (if any)	Prior to each use
Oxidation Reduction Potential Meter	Calibrate per manufacture's instruction	Daily prior to use
	Rinse probe with deionized or distilled water	After each reading
	Check batteries (if any)	Prior to each use
Turbidity Meter	Calibrate per manufacture's instruction	Daily prior to use
	Rinse probe with deionized or distilled water	After each reading
	Check batteries (if any)	Prior to each use

Prepared by: MCC2

Checked by: NMG1

Table 5-2
Recommended Field Corrective Action

Quality Control Activity	Acceptance Criteria	Recommended Corrective Action
Instrument Zero	Must Zero	Reset zero: if sample response, determine cause.
Initial Calibration	Standard concentration ±5% of expected value	Reanalyze standards; if still unacceptable, remake standards. If equipment malfunctions, notify manager.
Quality Control Check Standard	±5% of expected value	Reanalyze standard; if still unacceptable, remake standards or use new standards. If equipment malfunctions, notify manager.
Continuing Calibration	±5% of expected values	Reanalyze standard; if unacceptable, recalibrate equipment and rerun samples from last CC standard check. If equipment malfunctions, notify manager.

Notes:
% = percent
± = plus or minus

Prepared by: MCC2
Checked by: NMG1

Figures



Lake Superior

M-64

Porcupine Mountains Wilderness State Park

Carp Lake Township

Ontonagon Township

Greenland Township

Rockland Rd

M-38

M-26

Ontonagon County

Rockland Township

Gogebic County

Wakefield Township

Bergland Township

Matchwood Township

Stannard Township

M-28

McMillan Township

NOTES:
1. Base air photo from the USDA.
2. Horizontal coordinate system is NAD1983 UTM Zone, 16N, units in meters.
3. Hydrographic data from the USGS.
4. Road and boundary data from Michigan GIS Open Data and the USFS.
5. Site layout and infrastructure is based on 2019 White Pine North Copper Project PEA.

LEGEND

- Major Road
- Minor Road
- River/Stream
- Lake/Pond
- Municipal Boundary
- County Boundary
- Ottawa National Forest Boundary
- USDA Forest Service Owned Property
- Porcupine Mountains Wilderness State Park
- Proposed White Pine North Underground Mine Area
- Proposed Project Surface Extent (3,151 Acres)
- Historic Underground Mine Workings

Foth

N

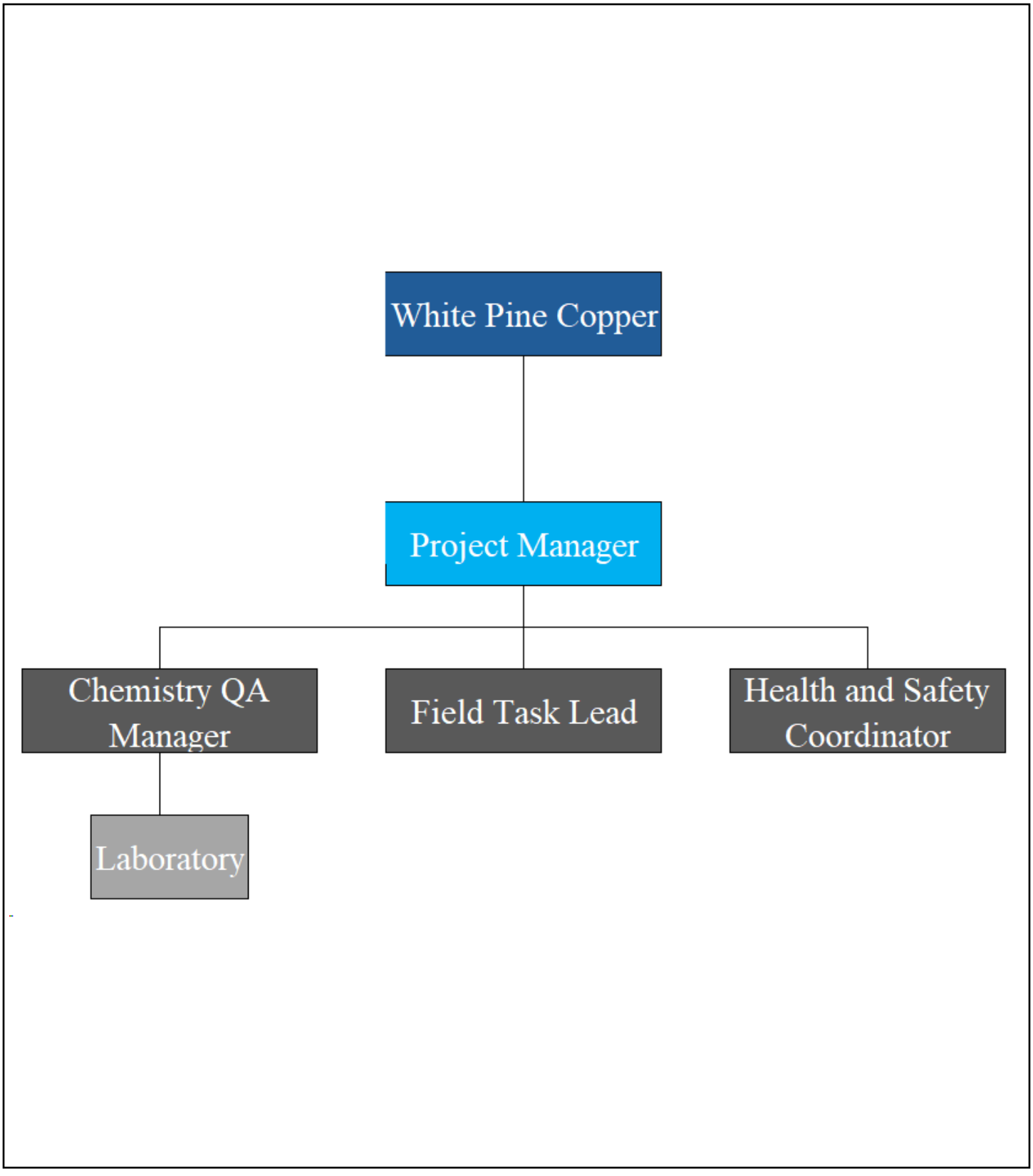
0 1.5 3 Miles

WHITE PINE COPPER LLC

FIGURE 1-1
PROJECT LOCATION MAP
ASSURANCE PROJECT PLAN
WHITE PINE NORTH
ONTONAGAN COUNTY, MICHIGAN

Date: JUNE 2024	Revision Date:	
Drawn By: BJW1	Checked By: MCC2	Project: 24W005

Path: Q:\White Pine Copper\24W005\GIS\aprx\QAPP.aprx Date: 7/18/2024



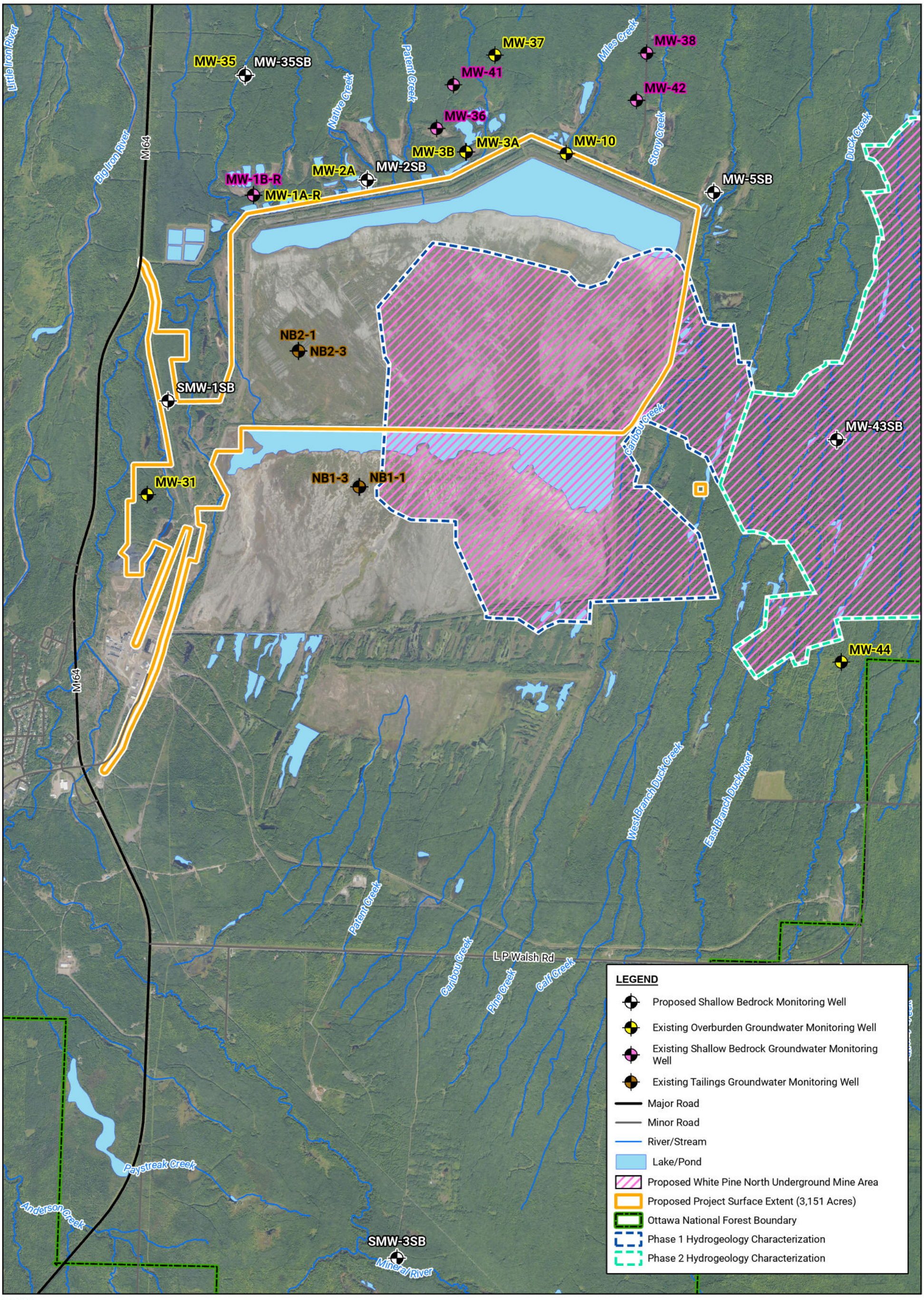
WHITE PINE COPPER LLC

FIGURE 1-2

ORGANIZATION CHART
ASSURANCE PROJECT PLAN
WHITE PINE NORTH
ONTONAGON COUNTY, MICHIGAN

Date: AUGUST 2024	Revision Date:	
Drawn By: BJW1	Checked By: MCC2	Project: 24W005

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NOTES:

1. Base air photo from the USDA.
2. Horizontal coordinate system is NAD1983 UTM Zone, 16N, units in meters.
3. Hydrographic data from the USGS.
4. Road and boundary data from Michigan GIS Open Data and the USFS.
5. Site layout and infrastructure is based on 2019 White Pine North Copper Project PEA.

This drawing is neither a legally recorded map nor a survey and is not intended to be used as one. This drawing is a compilation of records, information and data used for reference purposes only.

Foth

N

0 1,500 3,000 Feet

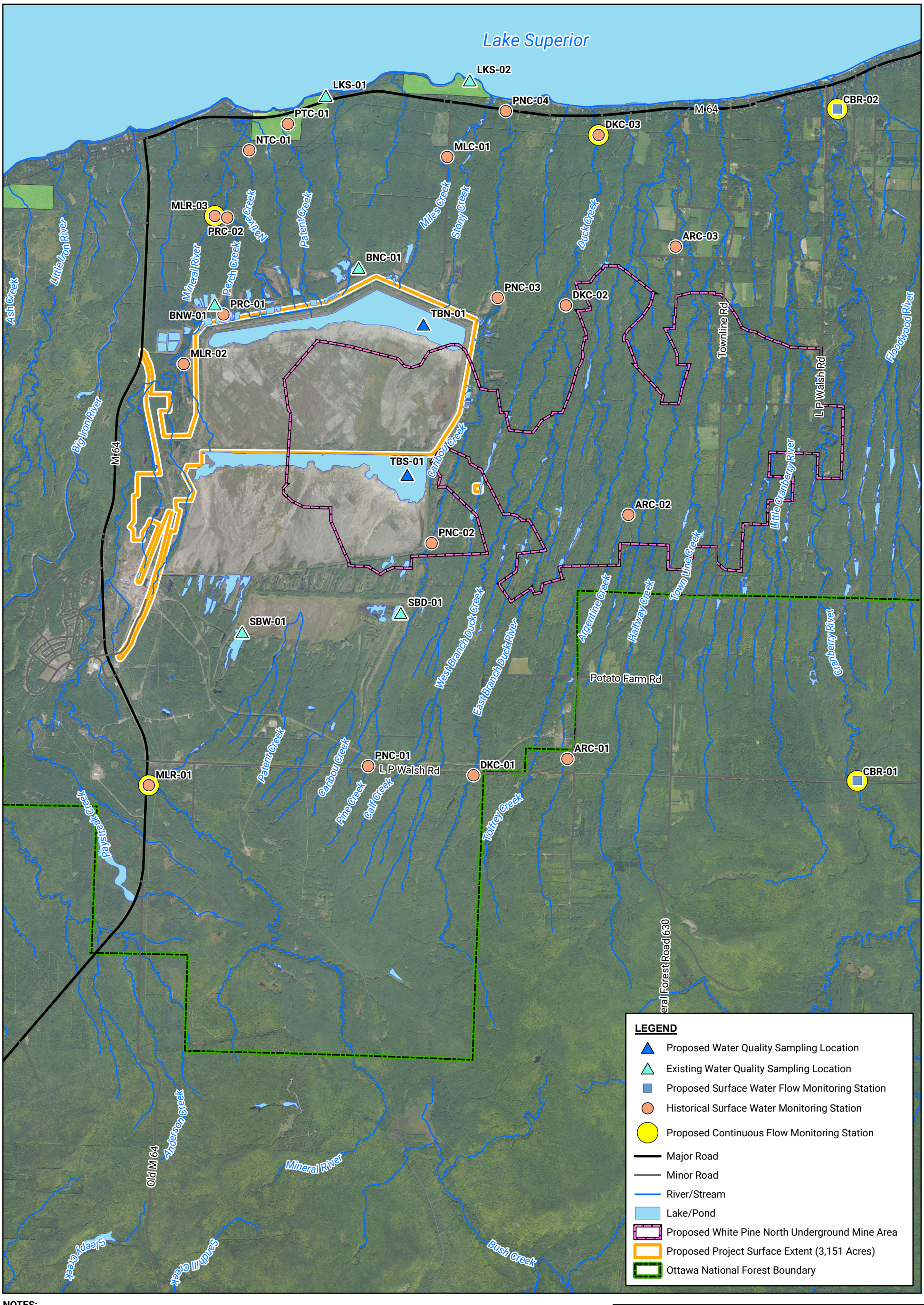
WHITE PINE COPPER LLC

FIGURE 2-1

GROUNDWATER MONITORING NETWORK
ASSURANCE PROJECT PLAN
WHITE PINE NORTH
ONTONAGON COUNTY, MICHIGAN

Date: JUNE 2024	Revision Date:	
Drawn By: BJW1	Checked By: MCC2	Project: 24W005

Q:\White Pine Copper\24W005\GIS\aprx\QAPP.aprx 7/18/2024 12:24 PM



NOTES:

1. Base air photo from the USDA.
2. Horizontal coordinate system is NAD1983 UTM Zone, 16N, units in meters.
3. Hydrographic data from the USGS.
4. Road and boundary data from Michigan GIS Open Data and the USFS.
5. Site layout and infrastructure is based on 2019 White Pine North Copper Project PEA.

This drawing is neither a legally recorded map nor a survey and is not intended to be used as one. This drawing is a compilation of records, information and data used for reference purposes only.

Foth

N

0 2,500 5,000 Feet

WHITE PINE COPPER LLC

FIGURE 2-2

SURFACE WATER MONITORING STATIONS
ASSURANCE PROJECT PLAN
WHITE PINE NORTH
ONTONAGON COUNTY, MICHIGAN

Date: JUNE 2024	Revision Date:		
Drawn By: BJW1	Checked By: MCC2	Project: 24W005	

Appendix A

Foth Standard Operating Procedures

SOP 2020 – Low-Level Mercury Groundwater Sampling
SOP 2021 – Low-Level Mercury Surface Water Sampling
SOP 2051 – Groundwater Purging & Sampling – Fixed Volume
SOP 2062 – Surface Water Sampling – Sampling from Shore
SOP 2101 – Stream Flow Site Selection Criteria & Measurement with Velocity-Area Method
SOP 2102 – Stream Flow Measurement Using Flowtracker 2 ADV
SOP 2103 – Stream Flow Measurement Using ADCP
SOP 2106 – Stage-Discharge Relation for Open Channel Flow
SOP 2107 – Staff Gauge Installation and Water Level Monitoring
SOP 2201 – AquaTroll® 600 Multiparameter Sonde
SOP 3113 – Data Verification, Validation, and Qualification
SOP 3207 – Field Log Book
SOP 3260 – Shipping and Packaging of Non-Hazardous Samples
SOP 3270 – Sample Chain of Custody

Foth Infrastructure & Environment, LLC

Standard Operating Procedure

Low-Level Mercury Groundwater Sampling

Introduction

The purpose of this Standard Operating Procedure (SOP) is to establish a standard procedure for Low Level Mercury Sampling of Groundwater. The general procedures to be utilized in obtaining low level mercury samples in groundwater are outlined below. Groundwater will be obtained via low-flow sampling, using dedicated or portable pumps.

Low level mercury analysis uses an extremely sensitive test method that can be affected by even slight contamination not related to the mercury level in the water. Contamination of samples or sample containers may originate from air, sampling personnel or contacted surfaces. To avoid contamination and to properly collect representative samples for low level mercury analysis, the persons obtaining the samples should have a team of at least two people with a proper understanding of potential sources of contamination. The team shall follow the "clean hands/dirty hands" procedure for sample collection. The incorporation of field blanks can help identify contamination and bias. Quality Control requirements established in the QAPP should meet the needs of the DQO. A field blank is a portion of mercury-free, laboratory supplied water that is processed through the full sequence of sampling steps.

References

U.S. Environmental Protection Agency (USEPA), Method 1669, "Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels," July 1996 (William A. Telliard, et al.).

U.S. Geologic Survey (USGS) Water Resource Division, "Low Level Collection Techniques and Species-Specific Analytical Methods for Mercury in Water, Sediment, and Biota," by Mark Olson and John F. De Wild reported in the USGS Water-Resource Investigations Report 99-4018B, 1999.

Telliard, William A., et. al, 1996. "Water Quality Criteria Levels." July1996.

Personnel Qualifications

Qualifications of sampling personnel are as directed in the Project Planning Document (PPD), Health & Safety Plan, and appointed by the Project Manager:

- All persons must be trained in this sampling technique.
- A minimum of two people are required to conduct sampling, but a third person is ideal for assistance depending on sample location or boat navigation.
  - "Clean hands" person.
  - "Dirty hands" person.
  - If sampling is conducted from a watercraft, the person operating the watercraft must have boating safety training.
- Additional Health and Safety Training Requirements:
  - All field personnel must have current CPR (Cardiopulmonary Resuscitation) and First Aid training.

- All field personnel must have satisfied Occupational safety and Health Administration (OSHA) training requirements (40 CFR 1910.120) if hazardous materials are expected.
- All field personnel must have satisfied Mine Safety and Health Administration (MSHA) requirements if working on a project site regulated by MSHA.

Equipment and Supplies

- Shipping container(s) for the sampling event to identify and protect bottles from possible sources of cross-contamination and breakage during storage and transportation.
- The correct quantity of properly cleaned and prepared glass or fluoropolymer (Teflon®) bottles (polyethylene bottles should not be used), stored in double self-seal plastic bags (remember blank(s) and extra bottles, if glass, to account for breakage. Note: Sample bottles will be pre-preserved in the laboratory.
- Mercury free lab water, for blanks, in containers and sealed in plastic bags.
- Provision for labeling samples (pre-labeled outer bags or other method).
- A sampling table and clean plastic sheeting to cover the table top and plastic clamps or other provision for retaining the plastic sheet on the table (the table may not be necessary if you don't have to set down bottles or you may set them down on another plastic-covered surface such as a cooler).
- Data log book, lab sheets, and chain of custody forms.
- Personal protective equipment that normally used when collecting samples at the sample collection site.
- Tyvek® (or equivalent) coveralls for sampling personnel. Note: Blue Tyvek® is NOT acceptable. No metal zippers, clasps, buttons, jewelry, etc. shall be exposed. Face masks or full face shields must be worn if any member of the sampling team uses tobacco products (smokes, chewing tobacco, etc.) or has mercury dental fillings or metal braces. Hoods (or equivalent) shall be worn to cover earrings.

Procedures

This is the basic procedure for collecting one sample. The procedure should give sampling personnel an idea which surfaces each person on the team may touch. To incorporate collection of field blanks into the procedure you may add a third person (second "clean hands") to the team or you may try a procedure where "clean hands" sets sample bottles down on previously spread plastic sheeting. Wells and tubing should be adequately purged, and care should be taked by "clean hands" not to touch any equipment after sampling commences.

Descriptions of possible field blank procedures follow the basic procedures for collecting samples.

1. All team members carry the equipment near the sampling site.
2. All members remove Tyvek® suits from protective bag and put them on. Face masks and hoods are to be donned, if applicable.
3. Prepare the sampling area for low-level technique to minimize contamination. Lay plastic sheeting down if needed for clean work area. Check wind and weather conditions. In field book, note operations of heavy equipment or other gas power equipment operating in area, exhaust from buildings, and any other potential sources of contamination. If any of the above conditions affect

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sample collection, the sampling event shall cease until conditions permit accurate sample collection.

4. Designate one member of the team as “clean hands” and the other as “dirty hands.” “Clean hands” may only touch the inner bag and sample bottle and performs the sampling. “Dirty hands” may NOT touch the inner bag or sample bottle but may touch anything else and performs tasks to assist “clean hands.”
5. “Dirty hands” opens a bag containing non-powdered gloves.
6. “Clean hands” removes a pair of clean gloves and puts them on.
7. “Dirty hands” removes a pair of clean gloves and puts them on.
8. “Dirty hands” removes a second pair of clean gloves and puts them on “clean hands” for double-gloving. “Clean hands” touches only the inner bag and sample bottle from this point forward. Prior to collecting the sample, the “clean hands” member should have fingers interlocked and in front of his/her face until sampling is performed.
9. “Dirty hands” removes an empty bagged sample bottle from the shipping container, closes the container, and opens the outer bag.
10. “Clean hands” opens the inner bag, removes the bottle, and folds the inner bag down into the outer bag.
11. “Dirty hands” seals the outer bag and puts it back in the shipping container.
12. “Clean hands” collects the sample by rinsing the sample bottle and cap three times and collecting the sample from the flowing stream.
13. “Dirty hands” retrieves the bags and opens the outer bag.
14. “Clean hands” reaches inside to re-open the inner bag, puts the sample bottle inside, and seals the inner bag.
15. “Dirty hands” seals the outer bag and places the bagged sample into the shipping container.
16. “Dirty hands” or third member of the team then records the sample bottle number with description and other relevant data.
17. “Clean hands” returns to a position which maintains contaminant-free sampling and prepares for filling the field blank.
18. Repeat Steps 9-20 for filling additional bottles, split samples, duplicates, or the field blank.

At the end of the sampling event, document the above sampling procedure in the project field notebook, including sampling team names. Note any possible sources of cross contamination that could affect the results during the sampling procedure.

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Standard Operating Procedure

Low-Level Mercury Surface Water Sampling

Introduction

The general procedures to be utilized in obtaining low level mercury samples in surface waters are outlined below. Grab samples will be obtained by submerging the sample bottle under the water surface interface prior to opening. Samples will be collected in a well-mixed area of flow, representative of the surface water being sampled.

Low level mercury analysis uses an extremely sensitive test method that can be affected by even slight contamination not related to the mercury level in the surface water. Contamination of samples or sample containers may originate from air, sampling personnel or contacted surfaces. To avoid contamination and to properly collect representative samples for low level mercury analysis, the persons obtaining the samples should have a team of at least two people with a good understanding of potential sources of contamination. The team shall follow the "clean hands/dirty hands" procedure for sample collection. The incorporation of field blanks can help identify contamination and bias. Quality Control requirements established in the QAPP should meet the needs of the DQO. A field blank is a portion of mercury-free, laboratory supplied water that is processed through the full sequence of sampling steps.

References

U.S. Environmental Protection Agency (USEPA), Method 1669, "Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels," July 1996 (William A. Telliard, et al.).

U.S. Geologic Survey (USGS) Water Resource Division, "Low Level Collection Techniques and Species-Specific Analytical Methods for Mercury in Water, Sediment, and Biota," by Mark Olson and John F. De Wild reported in the USGS Water-Resource Investigations Report 99-4018B, 1999.

"Water Quality Criteria Levels," July 1996 (William A. Telliard, et al.).

Personnel Qualifications

Qualifications of sampling personnel are as directed in the Project Planning Document (PPD), Health & Safety Plan, and appointed by the Project Manager:

- One person must be trained in this sampling technique.
- A minimum of two people are required to conduct sampling, but a third person is ideal for assistance depending on sample location or boat navigation.
    - "Clean hands" person
    - "Dirty hands" person
    - If sampling is conducted from a water craft, the person operating the water craft must have boating safety training.
- Additional Health and Safety Training Requirements:
    - All field personnel must have current CPR (Cardiopulmonary Resuscitation) and First Aid training.

- All field personnel must have satisfied Occupational safety and Health Administration (OSHA) training requirements (40 CFR 1910.120) if hazardous materials are expected.
- All field personnel must have satisfied Mine Safety and Health Administration (MSHA) requirements if working on a project site regulated by MSHA.

Equipment and Supplies

- Shipping container(s) for the sampling event to identify and protect bottles from possible sources of cross-contamination and breakage during storage and transportation.
- The correct quantity of properly cleaned and prepared glass or fluoropolymer (Teflon®) bottles (polyethylene bottles should not be used), stored in double self-seal plastic bags (remember blank(s) and extra bottles, if glass, to account for breakage. Note: Sample bottles will be pre-preserved in the laboratory.
- Mercury free lab water, for blanks, in containers and sealed in plastic bags.
- Provision for labeling samples (pre-labeled outer bags or other method).
- A sampling table and clean plastic sheeting to cover the table top and plastic clamps or other provision for retaining the plastic sheet on the table (the table may not be necessary if you don't have to set down bottles or you may set them down on another plastic-covered surface such as a cooler).
- Data log book, lab sheets, and chain of custody forms.
- Personal protective equipment that normally used when collecting samples at the sample collection site.
- Waders may be needed if entering a stream to collect samples.
- Tyvek® (or equivalent) coveralls for sampling personnel. Note: Blue Tyvek® is NOT acceptable. No metal zippers, clasps, buttons, jewelry, etc. shall be exposed. Face masks or full face shields must be worn if any member of the sampling team uses tobacco products (smokes, chewing tobacco, etc.) or has mercury dental fillings or metal braces. Hoods (or equivalent) shall be worn to cover earrings.

Procedures

This is the basic procedure for collecting one sample. The procedure should give sampling personnel an idea which surfaces each person on the team may touch. To incorporate collection of field blanks into the procedure you may add a third person (second "clean hands") to the team or you may try a procedure where "clean hands" sets sample bottles down on previously spread plastic sheeting.

Descriptions of possible field blank procedures follow the basic procedures for collecting samples.

1. All team members carry the equipment near the sampling site. If using a water craft, place equipment on plastic in water craft.
2. All members remove Tyvek® suits from protective bag and put them on (if used). "Dirty hands" may need to put on waders if accessing stream by wading. Face masks and hoods are to be donned, if applicable.
3. Prepare the sampling area for low-level technique to minimize contamination. Lay plastic sheeting down if needed for clean work area. Check wind and weather conditions. In field book, note

operations of heavy equipment or other gas power equipment operating in area, exhaust from buildings, and any other potential sources of contamination. If any of the above conditions affect sample collection, the sampling event shall cease until conditions permit accurate sample collection. Plan to enter the surface water, downstream from sample location. Sample location should be upstream of any culvert or bridge.

4. Designate one member of the team as "clean hands" and the other as "dirty hands." "Clean hands" may only touch the inner bag and sample bottle and performs the sampling. "Dirty hands" may NOT touch the inner bag or sample bottle but may touch anything else and performs tasks to assist "clean hands."

5. "Dirty hands" opens a bag containing non-powdered gloves.

6. "Clean hands" removes a pair of clean gloves and puts them on.

7. "Dirty hands" removes a pair of clean gloves and puts them on.

8. "Dirty hands" removes a second pair of clean gloves and puts them on "clean hands" for double-gloving. "Clean hands" touches only the inner bag and sample bottle from this point forward. Prior to collecting the sample, the "clean hands" member should have fingers interlocked and in front of his/her face until sampling is performed.

9. "Dirty hands" removes an empty bagged sample bottle from the shipping container, closes the container, and opens the outer bag.

10. "Clean hands" opens the inner bag, removes the bottle, and folds the inner bag down into the outer bag.

11. "Dirty hands" seals the outer bag and puts it back in the shipping container.

12. "Clean hands" enters the surface water and submerges the bottle at sample location. Sample bottle should be upright and pointed upstream into the flow.

13. "Clean hands" removes the bottle cap slightly from the bottle and bleeds surface water into the sample bottle at a slow rate. Air bubbles will indicate the bottle is filling. The sample bottle is partially filled and bottle cap tightened before bottle is removed from the water. Triple rinse is performed by shaking water in bottle and dumping back into the surface water, if the bottle is not pre-preserved. If sample bottle is pre-preserved, do not triple rinse bottle

14. After triple rinsing, the same procedure in Step 13 is used to collect sample; air bubbles will indicate the bottle is filling. When bubbles cease, the bottle is full--leaving a slight headspace.

15. "Clean hands" tightly screws the cap back onto the bottle under water. "Clean hands" returns to a position which maintains contaminant-free sampling while holding the sample bottle, awaiting next step.

16. "Dirty hands" retrieves the bags and opens the outer bag.

17. "Clean hands" reaches inside to re-open the inner bag, puts the sample bottle inside, and seals the inner bag.

18. "Dirty hands" seals the outer bag and places the bagged sample into the shipping container.

19. "Dirty hands" or third member of the team then records the sample bottle number with description and other relevant data.

20. "Clean hands" returns to a position which maintains contaminant-free sampling and prepares for filling the field blank.

21. Repeat Steps 9-20 for filling additional bottles, split samples, duplicates, or the field blank.

At the end of the sampling event, document the above sampling procedure in the project field notebook, including sampling team names. Note any possible sources of cross contamination that could affect the results during the sampling procedure.

Field Blank Collection Procedures

It may be useful to include a third person (second "clean hands") for field blank collection. Alternatively, the "clean hands" person may set sample bottles or field blank bottles down on previously spread, clean plastic sheeting. The field blank is for checking field contamination. Enough mercury-free water is needed to complete a triple rinse and fill sample bottle for sample collection. Document field conditions each time you prepare a field blank. If sources of contamination cannot be determined in the field, ask the lab to prepare a trip blank for low-level mercury to accompany the samples.

Note: A field blank is a volume of mercury-free water (usually shipped from the lab) that is processed through the full sequence of sampling steps and certified. Contrast this to a trip blank that is a bottle of mercury-free water (provided by the lab) that "goes along for the ride" but remains unopened at the sampling site.

Preservation and Storage for Low-Level Mercury

Ship collected samples to the lab following the procedures you and your lab agreed to.

1. Low level mercury samples shall be shipped/delivered on ice to the laboratory. In very cold weather, prevent the samples from freezing such as by shipping overnight.

2. Follow the instructions of your laboratory for chemical preservation, if any. Preservation of low level samples in the field is optional. Regulatory agencies recommend omitting field preservation, thereby eliminating that step as a potential source of contamination.

Note: Sample bottles that contain acid preservative may need to be shipped in accordance with the federal hazardous materials rules (49 CFR, Part 172).

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Standard Operating Procedure

Groundwater Purging & Sampling – Fixed Volume

Introduction

The purpose of this Standard Operating Procedure (SOP) is to establish a standard procedure to collect groundwater samples using the Fixed Volume Purging method. The objective of groundwater sampling is to collect samples that are representative of the aquifer in the surrounding geologic formation for evaluation of water quality, which may include field parameters, general chemistry, major cations and anions, metals, redox sensitive parameters, etc. Fixed Volume Purging and Sampling can be performed using a variety of different pumps and grab type equipment (ASTM, 2012).

This Fixed Volume Purging method may be used for wells that yield sufficient water to purge multiple well volumes without going dry (i.e., three to five well volumes, or as otherwise specified in the project specific sampling and analysis plan) prior to sample collection (USEPA, 2013). After purging the appropriate number of well volumes, measure water quality field parameters (i.e., pH, specific conductivity, turbidity, temperature, dissolved oxygen [DO], and oxidation-reduction potential [ORP]) prior to the collection of water samples for laboratory analysis. Water quality parameters are measured in the field at the well head with a flow-through cell or similar equipment (WDNR, 1996). If it is determined that collecting water quality parameters is not necessary, then disregard procedural steps that describe collecting water quality parameters.

References

ASTM International (ASTM). ASTM Designation D 6452 – 99, *Standard Guide for Purging Methods for Wells Used for Groundwater Quality Investigations*. 2012.

ASTM International (ASTM). ASTM Designation D 6699 – 01, *Standard Practice for Sampling Liquids Using Bailers*. 2006.

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Foth, 2021. *Measuring Static Water Level.* Standard Operating Procedure - #3272.

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Geotechnical Environmental Equipment (Geotech). *Reference Pages, Water Measure Tables*.

Ohio Environmental Protection Agency, State of Ohio (Ohio EPA). Technical Guidance for Ground Water Investigations, Chapter 10 Groundwater Sampling. February 2006.

Kansas Department of Health and Environment (KDHE). *Standard Operating Procedure – BER-01, Collection of Groundwater Samples at Known or Suspected Groundwater Contamination Sites*. January 1, 2011.

Minnesota Department of Agriculture (MDA). *Groundwater Monitoring Reporting Requirements*. March 2017.

United States Environmental Protection Agency (USEPA), EPA Region IV. *Groundwater Sampling Operating Procedure*. March 6, 2013.

Wisconsin Department of Natural Resources (WDNR), Bureau of Drinking Water and Groundwater. *Groundwater Sampling Field Manual*. September 1996.

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Personnel Qualifications

Qualifications of personnel are as directed in the Project Planning Document (PPD) (i.e., Sampling and Analysis Plan [SAP]), Health and Safety Plan, and appointed by the Project Manager (PM). A minimum of one person is required, who should be trained in this sampling technique. Additional persons may be required to complete sampling protocols where particular analytes are required (i.e., low-level mercury).

Equipment and Supplies

The selection of appropriate equipment depends on site conditions and project data quality objectives; equipment options for purging, measuring water quality, decontamination, and sampling are detailed below.

Purging Equipment

Dedicated Pumps and Tubing

- Dedicated equipment is used for sampling only the well in which the equipment is installed.
- Dedicated equipment should be used whenever possible for purging and sampling.
- Select appropriate pump based on well diameter, total depth of well, depth to water, the amount of water to be purged, and site conditions.
- Some pumps require a power source and a control box to regulate pumping rate. Examples include:
  - Submersible Pump (e.g., Grundfos® Redi-Flo2)
  - Bladder Pump

Non-dedicated, Portable Pumps

- Select appropriate pump based on well diameter, total depth of well, depth to water, the amount of water to be purged, and site conditions.
- Select appropriately sized tubing to pair with the chosen pump.
- Some pumps require a power source and a control box to regulate pumping rate. Examples include:
  - Submersible Pump (e.g., portable Grundfos® Redi-Flo2, whale pump, typhoon pump, tempest pump, cyclone pump, etc.)
  - Bladder Pump
  - Suction Pump (e.g., Peristaltic Pump)

Bailers

- Bailers are not recommended if other grab or pumping types are available because they are not practical for removing large volumes of water. In addition, surging of the bailer may disturb the sand pack, potentially elevating turbidity. Bailers may cause aeration when transferring sample (MDA, 2017).
- Bailers may be considered for purging and sampling where the static water level in the well is beyond the capabilities of a suction pump (approximately 25-30 feet below measuring point).

- A top filling bailer works well for sampling light, non-aqueous phase liquids (LNAPL).
- A double check valve bailer is able to effectively sample at discrete depths, and it should be considered when wanting to collect dense, non-aqueous phase liquids (DNAPL).
- If using a bailer, nylon line is necessary to attach to the bailer and use for retrieval. Unless the bailer is dedicated for use in one well, the nylon line should be discarded after use at each well.
- A flow-through cell cannot be used with a bailer. Water quality parameters may be collected by carefully filling a clean container with the bailer and then submersing the multiparameter probes. Some parameter reading may be compromised (such as dissolved oxygen) due to aeration of water.
- In-line filters are able to connect directly to certain bailers (please refer to the bailer's manufactures instructions). Pressure fed systems are recommended over gravity-fed systems (WDNR, 1996).
- Another option for field filtering when using a bailer is with the assistance of a peristaltic pump (or similar pump) that is used to pump bailed water through tubing into an in-line filter.
- Portable filtration can also be accomplished with a pressure or vacuum hand pump. It is recommended to use a pressure filtration device over the vacuum hand pump when available.

Water Quality Parameter Equipment

- A multiparameter probe capable of measuring project specific water quality parameters in a flow-through cell. Guidance regarding operation of the multiparameter probe can be found in the operator's manual, which should be consulted prior to equipment use.
- Adequate calibration solutions to perform calibration prior to sampling, and during and after the event if necessary.
- Examples of water quality multiparameter field probes include:
  - Aqua Troll 500 or 600
  - Hydrolab MS5X or Hydrolab Minisonde
  - Horiba U-50 Series
  - YSI mulitparameter water quality sonde
  - Aquaread Aquaprobe

Decontamination Materials

All non-dedicated equipment should be decontaminated between wells, using:

- Alconox® or equivalent solution (appropriate decontamination solution may vary based on contaminants of interest);
- Distilled or deionized water for rinsing;
- Bucket for containerizing and mixing solution; and
- Scrub brush for cleaning and removing debris.

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Other Important Equipment and Materials

- Water Level Indicator, capable of measuring to 0.01 feet (refer to Foth SOP Measuring Static Water Level #3272);
- Air compressor or air cylinder, if necessary;
- Appropriate Personal Protective Equipment (PPE), such as multiple pairs of disposable nitrile gloves (sufficient number so that they can be discarded after sampling each well), safety glasses, safety toe shoes, and any additional PPE as defined in the project specific Health and Safety Plan (HASP);
- Graduated cylinder, or container of known volume, and a stopwatch to measure pumping rate;
- Disposable 0.45 micron in-line filters if sampling for dissolved parameters;
- Appropriate sample containers;
- Trash container or bag;
- Disposable plastic sheeting or decontaminated bucket to place retrieval line of bailer in to avoid cross contamination;
- Electrical tape or similar;
- Cooler(s) with appropriate amount of cubed ice to keep samples cool;
- Container(s) in which to collect purged water, if necessary;
- Various tools: screwdrivers, wrenches, utility knife, measuring tape, extension cord, etc.;
- Hose clamps for creating a tight seal between tubing and non-dedicated pumps;
- Field log book or other appropriate field documentation; and
- Pen with waterproof ink.

General Procedures

General procedures described below include instructions to follow prior to sampling by all methods.

General procedures follow for purging and sampling with:

- a Dedicated Submersible Pump;
- a Non-Dedicated Submersible Pump;
- a Non-Dedicated Suction Pump; and
- a Non-Dedicated Bailer.

General procedures for equipment decontamination are listed, followed by the procedure for calculating well volumes and finally, important information to record when purging and sampling.

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Prior to Sampling

1. Communicate with the project manager about scope of upcoming activities and the proper strategy to be as efficient as possible in the field;
2. Familiarize yourself with sampling and analysis plan and project quality assurance plan;
3. Understand if the project requires the use of rental equipment, make sure to plan in advance for shipping and duration of use;
4. Coordinate with the lab and project manager to determine how the samples will efficiently get to the lab for analysis taking into consideration sample holding times;
5. Prepare equipment and materials including chain of custody, sample container labels, and appropriate documentation; and
6. Make sure that the proper power source(s) are charged or contain adequate fuel.

For Purging and Sampling with a Dedicated Submersible Pump

1. Open well; unlock and remove the well cap.
2. Decontaminate any non-dedicated equipment (including flow-through cell, parameter probes, associated hardware, water level indicator probes, etc.) that will be in contact with the well and groundwater (General Decontamination Procedures are described at the end of this SOP).
3. Insert the water level indicator probe and collect a static water level (refer to Foth SOP Measuring Static Water Level #3272).
4. Calculate the well volume that needs to be removed per the project specific sampling and analysis plan (Calculating Well Volumes is detailed at the end of this SOP).
5. Label sample bottles with the proper information including unique sample number, site/project name or other identifier, date of collection (record sample time in military time [e.g., 1300 instead of 1:00pm]), initials of field staff collecting samples, preservatives if present, and analysis required. Laboratory may supply pre-filled out labels; determine this during contracting with laboratory. Affix labels to bottles.
6. Connect the pumping rate controller to proper lead of the dedicated pump. Adjoin the discharge tubing tightly in place. Connect the pumping rate controller to the appropriate power source.
7. Turn down the pumping rate controller so that water is initially pumped at a slow and controlled rate. Turn on pump and increase rate if necessary to be constant and steady.
8. Record the time pumping was initiated. Measure time required to fill Graduated cylinder or container of known volume with stopwatch. Calculate the pumping rate and record.
9. Collect the discharged water for proper disposal, if required.
10. Calculate how long pumping will be performed based on pumping rate, or manually measure volume of water pumped out of well using graduated cylinder or container of known volume.
11. Connect the multiparameter YSI probe device to the flow-through cell.
12. Remove appropriate number of well volumes from the well. Slow pumping rate, then connect the discharge tubing to the flow-through cell adjoined with the multiparameter probe device (probes may be compromised if pumping at a high rate while is it connected to the flow-through cell). Allow

the flow-through cell to fill up and discharge water and wait for the probes to equilibrate with groundwater (may take 5-20 minutes). Record parameter values.

13. Disconnect the discharge tubing from the flow-through cell. Collect the unfiltered samples from the discharge tubing. Record time of sample collection. The pumping rate should be low enough to minimize sample aeration during collection. The discharge tube should not come into physical contact with the sample containers.

14. After unfiltered samples are collected, attach the disposable 0.45 micron in-line filter to the discharge tubing and sample the dissolved constituents.

15. Stop the pump and record pump stop time. Place samples on ice.

16. Disconnect all top leads from the dedicated pump. Put the well cap on and lock it. Dispose of any trash (such as in-line filter, tape, bubble wrap seals, label gloss, etc.).

17. Record all relevant site documentation (Field Documentation Information is listed at the bottom of this SOP) before leaving the well.

For Purging and Sampling with a Non-Dedicated Submersible Pump

1. Open well; unlock and remove the well cap. Slowly remove the well casing plug (J-Plug, PVC cap, etc.) and allow the water level to reach equilibrium with atmospheric pressure.

2. Decontaminate any non-dedicated equipment (including pump, flow-through cell, parameter probes, associated hardware, water level indicator probes, etc.) that will be in contact with the well and groundwater (General Decontamination Procedures are described at the end of this SOP).

3. Measure static water level. Measure total well depth if not known (refer to Foth SOP Measuring Static Water Level #3272).

4. Determine where the screened interval is located using prior documentation, if available, and determine the depth of middle of the screen, which is where the pump intake should be positioned.

5. Measure and cut the appropriate length of tubing to reach the desired depth (add roughly 5-10 feet of extra length to account for distance from well head to sampler). Avoid contaminating the tubing and well designated equipment.

6. Attach one end of the tubing to the discharge port on top of the pump and use a hose clamp to ensure a tight seal.

7. Install the pump to the desired depth (the middle of the screened zone). Slowly lower the pump either by the protected pump wire or by an attached safety cable, if available. Avoid lowering the pump by the tubing as the tubing and discharge port may disconnect. Secure the discharge tubing in place for pumping.

8. Secure the safety cable or protected wire to the protective casing to ensure the pump stays at the desired depth.

9. Calculate volume to remove from well per the project specific sampling and analysis plan (Calculating Well Volumes is detailed at the end of this SOP). Note that installing the pump and associated cable(s) will displace the water in the well, and it may take time for water level to re-equilibrate.

10. Connect the power source to the pump controller (if using) and connect the pump controller to the proper lead of the pump connection.

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11. Label sample bottles with the proper information including unique sample number, site/project name or other identifier, date of collection (record sample time in military time [e.g., 1300 instead of 1:00pm]), initials of field staff collecting samples, preservatives if present, and analysis required. Laboratory may supply pre-filled out labels; determine this during contracting with laboratory. Affix labels to bottles.

12. Turn down the pumping rate controller, if using, so that water is initially pumped at a slow and controlled rate. Turn on pump and increase rate if necessary to be constant and steady.

13. Record the time pumping was initiated. Measure time required to fill Graduated cylinder or container of known volume with stopwatch. Calculate the pumping rate and record.

14. Collect the discharged water for proper disposal, if required.

15. Calculate how long pumping will be performed based on pumping rate, or manually measure volume of water pumped out of well using graduated cylinder or container of known volume.

16. Connect the multiparameter YSI probe device to the flow-through cell.

17. Remove appropriate number of well volumes from the well. Slow pumping rate, then connect the discharge tubing to the flow-through cell adjoined with the multiparameter probe device (probes may be compromised if pumping at a high rate while is it connected to the flow-through cell). Allow the flow-through cell to fill up and discharge water and wait for the probes to equilibrate with groundwater (may take 5-20 minutes). Record parameter values.

18. Disconnect the discharge tubing from the flow-through cell. Collect the unfiltered samples from the discharge tubing. Record time of sample collection. The pumping rate should be low enough to minimize sample aeration during collection. The discharge tube should not come into physical contact with the sample containers.

19. After unfiltered samples are collected, attach the disposable 0.45 micron in-line filter to the discharge tubing and sample the dissolved constituents.

20. Stop the pump and record pump stop time. Place samples on ice.

21. Disconnect all leads from power cords, retrieve pump and associated tubing/cables from the well. Place the well casing plug (J-Plug, PVC cap, etc.) back on the well, put the well cap on and lock it. Dispose of any trash (such as in-line filter, tape, bubble wrap seals, label gloss, etc.).

22. Record all relevant site documentation (Field Documentation Information is listed at the bottom of this SOP) before leaving the well.

For Purging and Sampling with a Non-Dedicated Suction Pump

1. Open well; unlock and remove the well cap, slowly remove the well casing plug (J-Plug, PVC cap, etc.) and allow the water level to equilibrate with atmospheric pressure.

2. Decontaminate any non-dedicated equipment (including flow-through cell, parameter probes, associated hardware, water level indicator probes, etc.) that will be in contact with the well and groundwater (General Decontamination Procedures are described at the end of this SOP).

3. Measure static water level. Measure total well depth if not known (refer to Foth SOP Measuring Static Water Level #3272).

4. Determine where the screened interval is located using prior documentation, if available, and determine the depth of middle of the screen, which is where the pump intake should be positioned.

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5. Measure and cut the appropriate length of tubing to reach the desired depth (add roughly 5-10 feet of extra length to account for distance from well head to sampler). Avoid contaminating the tubing and well designated equipment.

6. Install tubing to the desired depth (the middle of the screened zone).

7. Secure the tubing to the well or protective casing, if necessary, to ensure well tubing depth is maintained and that if the tubing becomes detached from the silastic tubing it will not be lost.

8. Connect the installed tubing to the silastic or similar type tubing (approximately 1 foot length) that will attach to the pump rotor head. Insert the tubing with smaller outside diameter (tubing that was installed in the well) into the silastic tubing with matching inside diameter, creating an air tight connection.

9. Install a short length of tubing (length depends on field conditions - and should be determined by field staff) to the discharge end of the silastic tubing.

10. Check the pump vacuum direction to ensure that water is discharged from the outlet tubing (installed in step 9) and not pressurizing in the direction of the tubing intake. Turn down the pumping rate so that water will initially be pumped at a slow and controlled rate.

11. Connect the suction pump to the portable power source.

12. Installing the tubing will displace the water in the well. While the water is equilibrating, calculate volume to remove from well per the project specific sampling and analysis plan (Calculating Well Volumes is detailed at the end of this SOP).

13. Label sample bottles with the proper information including unique sample number, site/project name or other identifier, date of collection (record sample time in military time [e.g., 1300 instead of 1:00pm]), initials of field staff collecting samples, preservatives if present, and analysis required. Laboratory may supply pre-filled out labels; determine this during contracting with laboratory. Affix labels to bottles.

14. Turn down the pumping rate controller, if using, so that water is initially pumped at a slow and controlled rate. Turn on pump and increase rate if necessary to be constant and steady.

15. Record the time pumping was initiated. Measure time required to fill Graduated cylinder or container of known volume with stopwatch. Calculate the pumping rate and record.

16. Collect the discharged water for proper disposal, if required.

17. Calculate how long pumping will be performed based on pumping rate, or manually measure volume of water pumped out of well using graduated cylinder or container of known volume.

18. Remove appropriate number of well volumes from the well. Slow pumping rate, then connect the discharge tubing to the flow-through cell adjoined with the multiparameter probe device (probes may be compromised if pumping at a high rate while is it connected to the flow-through cell). Allow the flow-through cell to fill up and discharge water and wait for the probes to equilibrate with groundwater (may take 5-20 minutes). Record parameter values.

19. Disconnect the discharge tubing from the flow-through cell and collect the unfiltered samples from the discharge tubing. Record time of sample collection. It is important that the pumping rate is not too high that the sample water is being aerated as collection occurs and that the discharge tube does not come into physical contact with the sample containers.

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20. After unfiltered samples are collected, attach the disposable 0.45 micron in-line filter to the discharge tubing and sample the dissolved constituents.

21. Stop the pump and record pump stop time. Place samples on ice.

22. Disconnect all leads from power cords, retrieve pump and associated tubing/cables from the well. Place the well casing plug (J-Plug, PVC cap, etc.) back on the well, put the well cap on and lock it. Dispose of any trash (such as in-line filter, tape, bubble wrap seals, label gloss, etc.).

23. Record all relevant site documentation (Field Documentation Information is listed at the bottom of this SOP) before leaving the well.

For Purging and Sampling with a Non-Dedicated Bailer

1. Open well; unlock and remove the well cap. Slowly remove the well casing plug (J-Plug, PVC cap, etc.) and allow the water level to reach equilibrium with atmospheric pressure.

2. Decontaminate any non-dedicated equipment (including pump, flow-through cell, parameter probes, associated hardware, water level indicator probes, etc.) that will be in contact with the well and groundwater (General Decontamination Procedures are described at the end of this SOP). If using a disposable bailer, decontamination of the bailer will not be necessary.

3. Measure static water level. Measure total well depth if not known (refer to Foth SOP Measuring Static Water Level #3272).

4. Calculate volume to remove from well per the project specific sampling and analysis plan (Calculating Well Volumes is detailed at the end of this SOP).

5. Attach one end of the retrieval line (nylon line is recommended) to the bailer and the other end of the retrieval line to the protective well casing or to a nearby structure.

6. Measure out adequate length of retrieval line so that the bottom of the bailer will be positioned near the middle of the screened interval. Mark the retrieval line well so correct position is easily identifiable when lowering the bailer.

7. Lay disposable plastic sheeting around the base of the well or place a decontaminated bucket at the base of well to store the retrieval line and bailer and prevent cross contamination from ground surface.

8. Place the container(s) of known volume near the well for facilitate measuring the volume of purged water. If purged water is planned for disposal, plan to have adequate number of containers.

9. Place an additional decontaminated holding container near the well to receive bailed water and measure field parameters.

10. Label sample bottles with the proper information including unique sample number, site/project name or other identifier, date of collection (record sample time in military time [e.g., 1300 instead of 1:00pm]), initials of field staff collecting samples, preservatives if present, and analysis required. Laboratory may supply pre-filled out labels; determine this during contracting with laboratory. Affix labels to bottles.

11. Slowly lower the bailer into the well until it is completely submerged. Move bailer very slowly up and down to fill if necessary. Move slowly to minimize degassing, aeration, and turbidity in sample.

12. Empty water from the bailer into the container(s) of known volume to measure the volume of purged water.

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13. Remove appropriate number of well volumes from the well. Slowly bail water into the decontaminated container (pour slowly from the bailer to minimize sample agitation). Submerge the multiparameter probes, allow the probes to equilibrate (may take several minutes), and record water quality parameters. It may be necessary to continue to bail additional well water into the container for probe to equilibrate.

14. Begin sampling; record sample time.

15. Slowly lower the bailer into the well until it is completely submerged. Move bailer very slowly up and down to fill if necessary. Retrieve bailer when full.

16. Very slowly fill the unfiltered sample containers; pour slowly to minimize water agitation. Repeat as necessary to fill all sample bottles.

17. After unfiltered samples are collected, field-filtered samples should be collected, via one of a few ways:

    a. Bail water into a decontaminated container. Use a peristaltic pump with proper tubing, placing one end of tubing into the decontaminated container and connecting the in-line filter to the discharge end. Fill the appropriate sample containers with field filtered water.

    b. Directly connect the in-line filter to the bailer, if available (as described by the manufacturer's instructions) and fill the appropriate sample containers.

    c. Bail water into a decontaminated container. Transfer the bailed water using a portable vacuum or pressure filter to either "pull" or "push", respectively, water through the 0.45 micron filter. Fill the appropriate sample containers with field filtered water. This method should be only considered if the other options are not available.

18. Place samples on ice.

19. Dispose of any trash (such as in-line filter, tape, bubble wrap seals, label gloss, etc.).

20. Record all relevant site documentation (Field Documentation Information is listed at the bottom of this SOP) before leaving the well.

Decontamination

Field instruments and all non-disposable sampling equipment will be decontaminated before and after each use. Whenever possible, disposable sampling supplies (i.e., nitrile gloves) will be used to minimize the possibility of cross-contamination. The following procedures will be used for conducting decontamination of field instruments and sampling equipment:

1. Rinse or scrub equipment thoroughly using a phosphate-free, low-sudsing detergent solution (i.e., Liquinox or Alconox).

2. Rinse equipment with deionized water by submerging and/or spraying.

3. Allow equipment to air-dry.

Calculating Well Volumes

1. To calculate the number of gallons in a well volume, obtain these measurements:

    a. Well casing diameter (inches);

    b. Static water level (0.01 feet); and

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c. Total depth of well (*if there is a dedicated pump in the well, the depth of the pump should be used instead of the total depth of well).

2. Calculate one well volume in gallons (V) using one of the two methods below:

a. Equation (KDHE, 2011).

$$V = 0.041\ d^2 h$$

Where:

d = inside diameter of well in inches

h = height of water column (height of water column = Total depth of well – static water level)

Then, multiply value for one well volume (V) by total number of desired purged well volumes (typically 3 to 5).

b. Alternatively, refer to the table below:

Well Casing Diameter (inches)	Gallons per Foot of Depth (F)
1	0.041
1.5	0.092
2	0.163
2.5	0.255
3	0.367
4	0.653
4.5	0.826
5	1.020
5.5	1.234
6	1.469
7	2.000
8	2.611
9	3.305
10	4.080[1]

The values in the table can be used in the following formula to calculate one well volume, V, in gallons:

$$V = H * F$$

Where:

H = height of water column (height of water column = Total depth of well – static water level)

F = Factor for volume of 1-foot section of casing (gallons)

Then, multiply value for one well volume (V) by total number of desired purged well volumes (typically 3 to 5) (Ohio EPA, 2006).

[1] Information on table retrieved from Geotechnical Environmental Equipment (Geotech). Reference Pages, Water Measure Tables found at http://www.geotechenv.com/Reference_Pages/water_measure_tables.pdf

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Important Information to Record Associated with Purging and Sampling

- Field conditions and activities performed will be recorded in the Field Log Book and appropriate field forms as required (refer to Field Log Book SOP #3207).
- If photographs are taken, refer to Photograph Preparation SOP #3252 if using the Theodolite by Hunter Research and Technology phone app.
- Field logs should include the following information at a minimum:
  - Well identification;
  - Static water level;
  - Total depth of well;
  - Calculations (e.g., well volume calculations);
  - Date and time of purging;
  - Date and time of sampling;
  - Names of field personnel performing purging and/or sampling activities; and
  - Field observations, including weather conditions, site conditions, details associated with the purging and/or sampling efforts, water characteristics such as; odor, color, and/or appearance, any sampling complications.

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Standard Operating Procedure

Surface Water Sampling – Sampling from Shore

Introduction

The purpose of this Standard Operating Procedure (SOP) is to establish a standard procedure for the collection of analytical samples from the shore of surface waters. Sampling from shore presents accessibility challenges. The use of a dipper or pump tubing with an arm to allow for sample collection further from shore may be useful.

References

ASTM International (ASTM), 2019. Standard Practice for Sampling with a Dipper or Pond Sampler, D5358-93. *ASTM Annual Book of Standards*.

Foth Infrastructure & Environment, LLC (Foth), 2020. *Shipping and Packaging of Non-Hazardous Samples*, SOP 3260. 18 May 2020.

United States Environmental Protection Agency (USEPA), 2013. SESD [Science and Ecosystem Support Division] Operating Procedure Surface Water Sampling.

Personnel Qualifications

Personnel should be familiar with the reference documents, have read and understand the project Health and Safety Plan (HASP) and Quality Assurance Project Plan (QAPP).

Personnel participating in groundwater sampling should be familiar with this SOP and be proficient in the operation of the proper sample collection apparatus.

Personnel should have the Occupational Safety and Health Administration (OSHA) 40-hour Hazardous Waste Operations (HAZWOPER) training, and Mining Safety and Health Administration (MSHA) training, as applicable to specific client sites.

Equipment and Supplies

- Field Book.
- Sampling Plan.
- Dipper or peristaltic pump.
- Tubing for pump.
- Sample containers.
- Filters (if needed).
- Nitrile gloves.

Procedures

Preparation prior to sampling

- Prior to leaving the office, order and/or collect all necessary field equipment and supplies.
- Review QAPP, Sampling Plan, and HASP.
- Assemble required laboratory sample bottles, labels and gloves, and any needed sampling devices.

- Mark labels with sample number, sampler name, date and time of collection, analysis requested, and confirmation of a preservative, if present or to be added.
- Prepare the Chain of Custody.
- Attach labels to sample containers after they have been filled and sealed.
- Wear nitrile or appropriate gloves when collecting samples. Change gloves between sample locations or if they become damaged.
- Describe the nature of the sample location and adjacent areas.

Care should be taken not to disturb sediments on the bottom of the waterbody. Water should be collected as far from shore and in as deep of water as safely possible. Using a dipper or peristaltic pump in conjunction with a rigid extension rod is recommended. All equipment should be cleaned thoroughly prior to use and between each sampling site.

Sampling Method

The collection of certain samples may require adherence to a specific sampling protocol which may differ from this SOP. It is imperative that sediments on the bottom of the water are not disturbed during sampling. Therefore, it is recommended that collection of samples via wading be avoided.

Sampling with a Dipper

1. Collect water with a cleaned and rinsed dipper suitable for environmental sampling.
2. Pour water from the dipper into the sampling containers.
3. Immediately place sample container in a cooler with ice. If possible, put all glass bottle containers in plastic bags, as the label may come off during transport to lab. After the sample is collected, follow Foth SOP 3260, Shipping and Packaging of Non-Hazardous Samples.

Sampling with a Peristaltic Pump

The use of a peristaltic pump may be necessary if field filtering of the samples is required.

1. Assemble pump and install clean tubing for sampling.
2. Place tubing into the water, attaching a pole to the tubing during sampling to facilitate consistent depth placement may be necessary.
3. Allow water to flow through tubing for one to two minutes before filling bottles.
4. Fill bottles as directed.
5. Immediately place sample container in a cooler with ice. If possible, put all glass bottle containers in plastic bags, as the label may come off during transport to lab. After the sample is collected, follow Foth SOP 3260, *Shipping and Packaging of Non-Hazardous Samples*.

Direct Bottle Fill

First, determine if chemical preservatives are present in the sample container. Unpreserved sample containers may be slowly immersed in the water and allowed to fill. Sample containers with a preservative may not be immersed as they will lose the preservative into the water. Sample containers with preservative can be filled by first filling an unpreserved container using the method below, and then pouring the sample into the container with preservative.

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1. Immerse the sample bottle in water to a depth just below the surface or at a depth described in the work plan.
2. Hold the sample bottle as vertically as possible to allow the surface of the water to be collected.
3. Slowly unscrew the cap and allow water to slowly bubble into the sample container. As the water fills the container, the displaced air will bubble to the surface. The bottle will be filled with minimal headspace when the sample container stops bubbling.
4. Close the container by replacing its cap.
5. Tighten the cap.
6. Immediately place sample container in a cooler with ice. If possible, put all glass bottle containers in plastic bags, as the label may come off during transport to lab. After the sample is collected, follow Foth SOP 3260, *Shipping and Packaging of Non-Hazardous Samples*.

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Standard Operating Procedure

Stream Flow Site Selection Criteria & Measurement with Velocity-Area Method

Introduction

The purpose of this Standard Operating Procedure (SOP) is to establish a standard procedure for gathering data from flowing streams and constructed channels to use in flow rate calculations, and then to perform those calculations with the Velocity-Area Method. Streamflow measurements can be made in a variety of conveyances, including: rivers, streams, creeks, springs, drainage ditches, irrigation channels, industrial plant discharges, or any other surface feature characterized by predominantly one-dimensional flow and open channel conditions (as opposed to a closed or full conduit). This procedure is applicable to streamflow measurements made via wading, bridges, cableways, and boats.

This SOP defines methods for calculation of volumetric flow rates for water in open channels and streams using measurements of velocity, flow depth, and cross-sectional area. This procedure is largely based on the use of current meters to measure flow velocity. Note that a variety of current meters are available for stream flow measurement, including both mechanical and hydroacoustic meters. Hydroacoustic meters include acoustic doppler velocimeters (ADVs) and acoustic doppler current profilers (ADCPs). While Foth contains separate SOPs specific to the use of ADV meters (*Foth Standard Operating Procedure #2102*, Stream Flow Measurement Using Flowtracker 2 ADV) (Foth, 2021a), and ADCP meters (*Foth Standard Operating Procedure #2103*, Stream Flow Measurement Using ADCP) (Foth, 2021b), the methods used with those meters follow the velocity-area principles contained in this SOP. In addition, this SOP includes the Float (Surface) Method when the use of a current meter is not possible due to flow conditions.

Furthermore, this SOP contains site selection criteria for open channel/stream flow measurement locations, which are applicable to the velocity-area method regardless of the method used to record velocity. This SOP also contains guidance on measuring flow when the section line is not orthogonal to stream flow, when negative flows are recorded, when alternative methods to wading are required (e.g. from bridge or boat), and when ice conditions exist.

References

ASTM Standard D3858-95, 2014. "Standard Test Method for Open-Channel Flow Measurement of Water by Velocity-Area Method," ASTM International, West Conshohocken, PA, 2014, DOI: 10.1520/D3858-95R14, www.astm.org.

ASTM Standard D5089-95, 2014. "Standard Test Method for Velocity Measurements of Water in Open Channels with Electromagnetic Current Meters," ASTM International, West Conshohocken, PA, 2014, DOI: 10.1520/D5089-95R14, www.astm.org.

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ASTM Standard D4409-95, 2014. "Standard Test Method for Velocity Measurements of Water in Open Channels with Rotating Element Current Meters," ASTM International, West Conshohocken, PA, 2014, DOI: 10.1520/D4409-95R14, www.astm.org.

Foth, 2021a. *Foth Standard Operating Procedure #2102*, Stream Flow Measurement Using Flowtracker 2 ADV.

Foth, 2021b. *Foth Standard Operating Procedure #2103*, Stream Flow Measurement Using ADCP.

Foth, 2021c. *Foth Standard Operating Procedure #2104*, Culvert Flow Rate Monitoring.

Turnipseed, D.P., and Sauer, V.B., 2010. "Discharge Measurements at Gaging Stations," Techniques and Methods Chapter 8 of Book 3, Section A (3-8A), U.S. Geological Survey, Reston, VA. (Also available at http://pubs.usgs.gov/tm/tm3-a8/.)

U.S. Forest Service, 1994. "Stream Channel Reference Sites: An Illustrated Guide to Field Technique". General Technical Report RM-245.

U.S. Geological Survey, 1982. "Measurement and Computation of Stream Flow: Volume 1 Measurement of Stage and Discharge", Water Supply Paper 2175.

Personnel Qualifications

A minimum of one qualified person is required to complete field measurements. A qualified person shall be someone who is formally trained in hydrology via an Accreditation Board for Engineering and Technology (ABET)-accredited engineering college or university and experienced in making open channel flow measurements. A qualified person may also be a technician lacking formal college training in hydrology but whom has been formally trained in open channel flow measurements using the procedures described in this SOP.

Personnel performing open-channel flow measurements shall have access to the project Health and Safety Plan (HASP). Note that the HASP may require a minimum of two people to be present when near water features such as rivers and streams.

Additional Health and Safety Training Recommendations:

- Field personnel shall have current CPR (Cardiopulmonary Resuscitation) and First Aid training.
- Field personnel shall have satisfied Occupational Safety and Health Administration (OSHA) training requirements (40 CFR 1910.120) if hazardous materials are known to be or may be present at the site.
- Field personnel shall have satisfied Mine Safety and Health Administration (MSHA) safety training requirements prior to making open channel flow measurements on a project site regulated by MSHA.

Equipment and Supplies

Required equipment will vary according to the measurement method and may include the following:

- Flat tape measure
- Current meter (rotating element, electromagnetic, and acoustic current meters can be used in conjunction with this procedure)

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- Graduated wading rod (United States Geological Survey (USGS)-style top-setting wading rod or conventional graduated wading rod can be used; example of top-setting style is a Rickly 12-foot Breakdown Top Set Rod. Wading rods are available from Rickly Hydrological, Hydrological Services America, Ben Meadows, and others)
- Weighted and graduated sounding reel or sounding line (optional, depending on flow conditions)
- Metal or wood stakes
- Hammer or fence-post driver
- Rake (optional)
- Waterproof marker or pen
- Field Log Book and Form(s)
- Stop Watch
- Bucket
- Float (buoyant and biodegradable, such as wood/branch, pine cone, orange) (optional, if using Float (Surface) Method)
- Hip or chest waders
- USGS-approved personal flotation device
- Rain gear, if applicable
- Ice fishing auger (if ice cover is expected)

Procedures

Procedures below for determining channel/stream flow rate are organized into the following subsections:

- Channel/Stream Flow Rate - Site Selection Criteria
- Channel/Stream Flow Rate - General Measurement Procedures
- Channel/Stream Area and Flow Velocity - Field Measurement Procedures
- Channel/Stream Flow Rate - Calculations

Channel/Stream Flow Rate - Site Selection Criteria

Selection of stream flow sites will ideally meet the criteria listed below. Rarely will a site meet all of these criteria, so professional judgment must be exercised in site selection. Sites are often pre-selected from aerial photographs and topographic maps. If field observations of the pre-selected stream flow sites violate priority criteria, the project manager (PM)/ project discipline leader (PDL) should be notified, and the site location ID and violated priority criteria should be noted in the field book. At the discretion of the PM/PDL, this information will be used to optimize (i.e., relocate, remove, etc.) the stream flow measuring location.

1. The stream flow site is readily and safely accessible for ease of installation and operation of the flow meter during any season (i.e., high flow or low flow).

2. The stream flow site provides measurable flow during most months of the year, and allows for both high and low flows to be measured.

3. The total flow is confined to one channel at all stages, and no flow bypasses the site as subsurface flow.

4. Stream velocities are, for the most part, greater than 0.5 feet per second, and depths are greater than 0.5 feet.

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5. As a rule, the stream should be straight for a distance upstream and downstream of the measuring cross-section that is the greater of the two: 1) at least three channel widths (ASTM Standard D3858-95, 2014), or 2) at least 300 feet (USGS, 1982).

6. The stream flow site is at least 100 feet upstream/downstream of a narrowing or widening of the stream channel due to natural conditions (i.e., tree fall, meandering stream, confluences with other streams) or unnatural conditions (i.e., bridge), or from confluence with another stream.

7. The stream flow site is at least 5 diameters upstream and/or 10 diameters downstream of any culvert. If multiple culverts are present, use the diameter of the largest culvert to determine the upstream and/or downstream stream flow site location. Note: If a culvert is the target for flow measurement, please refer to *Foth Standard Operating Procedure #2104*, Culvert Flow Rate Monitoring (Foth, 2021c) for instruction.

8. Banks are permanent, high enough to contain floods, and are free of brush.

9. The stream flow site contains relatively uniform flow, free of eddies, slack water, large rocks, piers, weeds, or other obstructions that will cause excessive turbulence or create a vertical component in measured velocity.

10. The stream channel and stream bed, in the vicinity of the stream flow site, are stable (i.e., not subject to scour, fill, vegetative cover or aquatic growth) during most months of the year.

11. The stream flow site is at or near a gauging station or staff gauge to obtain concurrent surface-water discharge data required for computing constituent-transport loads, and to determine relationships between discharge and constituent concentrations.

Channel/Stream Flow Rate - General Measurement Procedures

1. The procedure for making velocity measurements in streams and open channels using a rotating element current meter is provided in ASTM D4409-95. ASTM D4409-95 is incorporated by reference to this procedure. Methods detailed in ASTM D4409-95 shall be followed when using rotating element current meters for velocity measurements in open channels and streams.

2. The procedure for making velocity measurements in streams and open channels using an electromagnetic current meter is provided in ASTM D5089-95. ASTM D5089-95 is incorporated by reference to this procedure. Methods detailed in ASTM D5089-95 shall be followed when using electromagnetic current meters for velocity measurements in open channels and streams.

3. The procedures for collection of field measurements and calculation of flows in open channels characterized by flow that is predominantly one-dimensional using a current meter is provided in ASTM D3858-95. ASTM D3858-95 is incorporated by reference to this procedure, and is summarized below in the 'Field Measurement Procedures' and 'Calculations' sections of this SOP. When the direction of flow is known or believed to vary substantially as a function of depth, rotating element and electromagnetic current meters shall not be used for the measurement of velocity. Rather, velocities shall be measured using acoustic Doppler current profiling (ACDP) devices and methods.

4. *Flow Angle:* Whenever possible, subsection width, depth, and velocity measurements shall be made along a section line (or bridge) that is oriented orthogonal to the velocity vector for the majority of the streamflow. When the predominant velocity vector is not normal to the measuring section, a correction shall be applied to the velocity measurement as described on page 24 of Turnipseed, 2010. Velocity values used to calculate flux for a subsection shall be calculated as $V_O = V_M * \cos(\alpha)$, where V_O is the velocity orthogonal to the measuring section (used to estimate discharge), V_M is the maximum velocity

in the channel or stream (measured using current meter), and α is the angle between the maximum velocity vector and the orthogonal to the measuring section.

5. *Wading:* When stream depths and flow velocities are modest, depth and velocity measurements shall be made via wading. As a "rule of thumb", wading measurements are safe when the product (multiplication) of water velocity (feet per second) and depth (feet) is less than 10.

   When wading is possible, a pre-marked tag line shall be set across the stream and used to subdivide the stream into measurement segments/subsections as described in ASTM D3858-95 and summarized in the 'Field Measurement Procedures' section of this SOP. Stream depths shall be recorded for each stream segment/sub-section. Depth measurements shall be made using a graduated wading rod. A top-setting wading rod shall be used in all instances because a top-setting rod simplifies the measurement of depths and the positioning of the current meter at proper depths for velocity measurements. Refer to the instructions provided for the specific model of top-setting rod used for the proper method of measuring stream depth and setting of current meter depth.

   Velocity measurement depth(s) shall be calculated based on the stream depth and the total depth fraction specified by the chosen method (as described in ASTM D3858-95 and summarized in the 'Field Measurement Procedures' section of this SOP). The technician should stand well to the side and slightly downstream of the meter as readings are taken, and avoid disturbing the streambed beneath the measuring point.

6. *Alternate Methods to Wading:* When stream depth or velocity exceeds limits for safe wading, measurements of depth and velocity may be made using current meters via alternate methods. As a "rule of thumb", wading is unsafe when the product of water velocity (feet per second) and depth (feet) exceeds 10. Alternate options to wading include measurements made from a suspended cableway, from a bridge, and from a boat. These methods are described briefly below; additional detail can be found in ASTM D3858-95 and on the appropriate pages listed of Turnipseed, 2010.

   6.1 *Current-Meter Measurements from Cableways:* Procedures for use of cableways can be found in ASTM D3858-95 and on page 27 of Turnipseed, 2010.

   6.2 *Current-Meter Measurements from Bridges:* Measurements from bridges are made by suspending the current meter on a handline or on a line attached to a sounding reel mounted on a bridge crane or dolley. A sounding weight is suspended below the meter to hold it in position and as a method of obtaining water depth. Measurements can be made from either the upstream or downstream side of the bridge, although the upstream side is generally preferred.

   Additional details and considerations on measurements from bridges are as follows:

   - If measurements are to be made from a bridge, a bridge should be selected that is orthogonal to the bulk streamflow velocity vector. If the bridge is not orthogonal to the velocity vector, the technician shall correct measured velocities using the method described in Item #4 above.

   - Bridge piers will often cause horizontal flow angles that must carefully be measured. Piers also often cause rapid changes in the horizontal-velocity distribution in the section. Whether or not to include the area of the bridge pier from the area of the measurement cross section depends primarily on the relative locations of the measurement section and the end of the pier.

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- Measurements from a bridge can be made using a wading rod if the bridge deck is close to the stream and the stream is relatively shallow.

- If the distance to the water surface and/or channel bottom exceed the reach of a wading rod or a standard wading rod (which are often longer in length than top-setting wading rods and may be used to make depth measurements and position velocity meters when making depth and velocity measurements from a bridge), measurements made from a bridge may require use of a sounding cable and weights. Depth measurements and positioning of velocity meters using sounding cables and reels in the presence of swift water is complicated by the deflection of the sounding weight and cable. Use of sounding cables for depth measurements and meter positioning from bridges is permitted only when velocities are modest such that deflection of the cable is minimal.

- *Water Depth:* When making measurements from a bridge with the use of a sounding cable and reel, the sounding cable shall be used to make and record depth soundings for all sub-sections prior to making velocity measurements. Depth soundings shall be made by measuring and recording the distance to the water surface and then the distance to the bottom of the channel. When these measurements are made for a particular subsection, the technician shall establish a fixed reference point for each measurement in a subsection. The reference point from one subsection to another need not be at the same absolute elevation. However, the reference point *must* be the same for both measurements (distance to water surface and distance to channel bottom) for each individual subsection. Measure and record each depth, and then subtract the distance to the water surface from the distance to the channel bottom to obtain the stream or channel depth. Use of a sounding-reel bridge crane or dolly simplifies depth sounding and meter positioning from bridges. Use of a crane or dolly also improves accuracy of depth soundings and meter positioning for bridge-access streamflow measurements.

- *Water Velocity:* Calculate the distance between the sounding weight and the velocity meter using the measured depth and the appropriate fraction for the method being used. Fix the meter the appropriate distance from the weight. Lower the sounding cable and weight into the water until the weight contacts the stream bottom. Maintain this position until the velocity measurement is completed. Adjust the distance between meter and weight and repeat for remaining required velocity measurement depths. Record each velocity measurement.

Additional detail on measurements from bridges can be found in ASTM D3858-95 and on page 28 of Turnipseed, 2010.

6.3 *Current-Meter Measurements from Boats:* Small, lightweight boats, manipulated by outboard motors, oars, or anchor lines, can be used as a platform for making flow measurements. Measurements can be made using either a wading rod or sounding cable/reel and weights, depending on flow depth and conditions. It should be noted that while automatic, computerized methods are available using mechanical current meters, the practice of recording stream flows by boat (whether using manual or automated mechanical current meters) is being almost entirely replaced in common practice by the use of the ADCP method.

Additional details and considerations on measurements from boats are as follows:

- Measurements made from a boat require two technicians. One technician operates the boat and is responsible for occupant safety and positioning the boat at the required subsection centers across the measuring section. The second technician makes and records depth and velocity measurements.

- Measurements from a boat are often conducted by setting tag line on both streambanks for lateral positioning and subsection width measurement. Setting of the tag line precludes complications arising from a measurement section that is oblique to the bulk streamflow velocity vector.

- Measurements are compatible with a wading rod for depth sounding and meter positioning, unless stream depths exceed 8 to 10 feet. Use of a wading rod is easier, quicker, and more accurate than use of a sounding cable/reel and weight.

  When making depth sounding measurements from a boat using a wading rod, the boat will move in the vertical plane due to water movement and movements within the boat. The technician making the measurements shall strive to keep the wading rod fixed firmly against the channel bottom. This will eliminate the need to interpret depth variations caused by movement of the boat.

- For deep settings wherein a wading rod is too short, use of a meter and sounding weights with cable/reel is required. The meter and sounding weights are often suspended by a cable attached to a boom extending over the bow of the boat, or can be held by the technician. However, the sounding cable and attached weight shall be deployed into the stream such that fluctuations in the boat elevation do not raise the weight away from the channel bottom. Using this approach, read the channel depth from the sounding cable at the water surface, and record the measured depth. Velocity measurement procedures are similar to those discussed previously under the Section 6.2 (Bridges).

Additional detail on measurements from boats can be found in ASTM D3858-95 and on pages 32-34 of Turnipseed, 2010.

7. *Ice Cover:* Stream flow measurements can also be made in frozen streams when ice is of sufficient thickness to permit foot access. Note, however, that ice thickness is extremely variable when the water beneath the ice is flowing, as is the case for streams. Accordingly, measurements of stream discharge under frozen, iced-over conditions are considered dangerous and generally not recommended. For instances where this practice will be used, the technician shall be accompanied by a partner, and both persons shall be trained in ice safety and ice/water rescue.

   Additional details and considerations on measurements with ice cover are as follows:

   - An ice auger or chisel is required to gain access to the stream through the ice. Subsection width should be kept relatively large. If not, the closely spaced access holes will weaken the ice surface, increasing the risk of the technician falling through the ice. Note on narrow, shallow streams, it may be simpler to remove all of the ice in the cross section.

   - The presence of an ice sheet on top of the water surface affects the water depth computation. The effective depth, or water depth beneath the ice, is computed by subtracting the ice depth from the total depth from the ice surface to the stream bed. The segment/subsection computation is then made by multiplying the effective depth by the width, which is obtained in the same manner as in the open-water wading measurements discussed below in this SOP.

   - The presence of ice can also have the effect of an added channel roughness and resistance to flow, altering the shape of the vertical-velocity profile. When velocity is obtained by the two-point method (0.2 and 0.8 depths), the observations are used as in the open-water measurement. However, if the six-tenths depth method is used, a correction coefficient of 0.92

is applied to the velocity observations. Alternatively, a velocity observation can be taken at the 0.5 depth and a coefficient of 0.88 can be applied.

Additional details regarding the measurement of stream discharge in ice-covered streams and open channels is provided in ASTM D3858-95 and on pages 29-31 of Turnipseed, 2010.

8. *Negative Flows:* If negative flow velocities are measured in any portions of the stream, the following procedure should be used to supplement the calculation procedure detailed in ASTM D3858-95:

    a. Divide the subsection where the negative flow was observed into three equal-width subsections.

    b. Make and record stream depth soundings at the center of each newly-defined subsection, as shown in Figure 1.

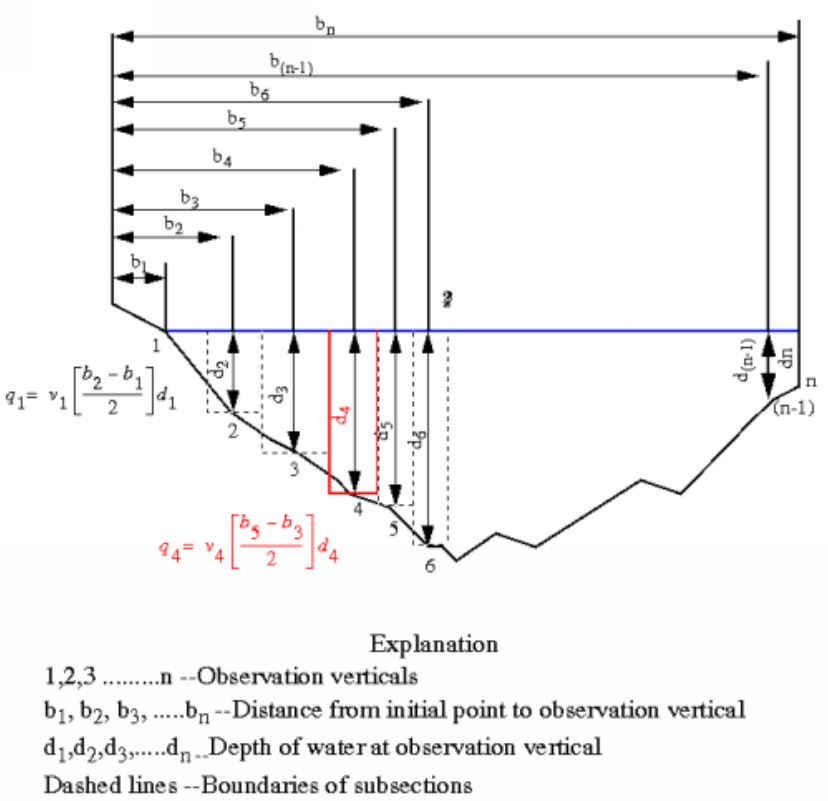
    c. Make and record velocity measurements at depths appropriate for the chosen method at the centers of each newly-defined subsection, as shown in Figure 1.

    d. Compute the discharge for each subsection, as described in the 'Calculations' section of this SOP.

Channel/Stream Area and Flow Velocity - Field Measurement Procedures

The following diagram (Figure 1) shows the measurements required for stream/discharge flow using a current velocity meter and/or the Float (Surface) Method. All measurements shall be recorded on the attached field form (note that two forms are available, one if using a current meter and one if using the Float (Surface) Method). Position, weather, wind direction and speed, general stream condition (e.g., turbid, clear, low level, floating debris, water temperature, type of streambed material, etc.), relative observations, instrument problems, or public interaction shall be recorded in the field book.

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$$Q = \sum_i^n q_i = \sum_i^n v_i a_i = \sum_i^n v_i (w_i d_i)$$

where

Q = total stream discharge
q_i = discharge in subsection i
v_i = mean flow velocity normal to subsection i
a_i = crossectional area of subsection i
w_i = width of subsection i

$$= \begin{cases} \frac{b_2 - b_1}{2} & \text{if } i = 1; \\ \frac{b_{i+1} - b_{i-1}}{2} & \text{if } 2 \le i \le n-1; \\ \frac{b_n - b_{n-1}}{2} & \text{if } i = n \end{cases}$$

d_i = depth of subsection i
b_i = distance from shoreline datum to center of subsection i
n = number of subsections dividing the stream crossection

Figure 1 - Stream Flow Measuring Cross-Section (showing 'Mid-section Method' for calculating stream flow).

As additional explanation for Figure 1, the "Observation Verticals" are represented by the "Station Number" in the field form. The "Initial Point" is indicated as "Station 0" in the field form; a stake should be driven at this point. The "b" variable is recorded as the "Station Distance" in the field form. The "d" variable is recorded as the "Station Depth" in the field form. The dashed lines represent the width calculations used in the 'Mid-Section Method' used to calculate total flow rate. Note that the 'Mean-Section Method' is also used as an option to calculate total flow rate, as described in the 'Calculations' section of this SOP. Either the 'Mean-Section' or 'Mid-Section' methods can be used to calculate total flow; however the field data collection requirements are identical between the two methods. Additionally, the Float (Surface) Method contained in this SOP references this figure since either the 'Mean-Section' or 'Mid-Section' methods are again used to determine the stream cross-sectional area.

Field Measurement Procedures

1. Preparation prior to sampling
    a. Review the HASP with field personnel.
    b. Check current weather conditions. Stream gauging may be hazardous during extreme weather and icy conditions may require additional equipment.
    c. Check the current meter for signs of wear or damage and ensure that the battery is fully charged, if applicable. Inspect other equipment to ensure all essential components are in proper working order. Replace equipment that is damaged, worn, or of questionable integrity.
2. Select/verify the stream flow measuring location using the criteria identified in the 'Site Selection Criteria' section of this SOP. Record the location using the handheld GPS.

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3. From the stream bank, determine the direction of flow and record it as a cardinal direction (i.e., N, NE, S, SW, etc.) in the field book (use the GPS, compass, or phone compass application to determine direction). From the stream bank, determine which bank Station 0 is located on (left or right bank when looking downstream) and record in the field book and field form.

4. From the stream bank, identify a transect line through the stream that is approximately perpendicular to the direction of flow. If possible, drive a stake on dry land adjacent to the stream bank, to be used for subsequent stream flow readings to maintain consistency throughout the study period (if a stake is not possible, the use of detailed notes and a camera can help re-occupy the same location).

   The stake should be located landward of the expected high water mark. Fix the starting end of the flat tape to the stake (or equivalent, if driving a stake is not possible). This will represent Station 0, and the tape reading will be 0.0. The distance from the stake/tape start point to the stream water edge (Station 1) will be distance "b_1" on Figure 1. Spool out the flat tape across the stream, perpendicular to the stream flow direction, and fix the flat tape to the opposite stream bank. The water edge on the opposite stream bank will be distance "b_n" on Figure 1.

5. Based on the total width of the stream identified from the flat tape in the previous step, determine a regular interval to divide the stream into equal width subsections. The overall accuracy of the measurement is generally increased by increasing the number of subsections. Generally 25 – 30 subsections, even for large channels/streams, are adequate depending on the variability and complexity of the flow and cross section. Fewer subsections can be used with a smooth cross section and uniform velocity distribution, especially in narrower streams.

   As a general rule, enough subsections should be established to prevent more than 10% of the total discharge from passing through any one subsection. For example, for a 60-foot channel, use no less than 6-foot wide subsections (60 *0.10 = 6). The following can also be used as a guide to determine the subsection widths:

   a. Small stream channel (12 feet wide or less) – use 1-foot wide subsections.
   b. Medium stream channel (16-30 feet wide) – use 2-foot wide subsections.
   c. Large stream channel (30 feet or large) – use 3-foot wide subsections.

   Finally, the end sections (the calculation sections involving both stream edges) should be chosen to have small widths, in an effort to minimize errors resulting from edge effects.

6. Once the interval width of each subsection has been identified, the number of stations will be known. For example, in a 16-foot wide channel, Stations 1-9 will be used to collect depth and velocity measurements. Note that Station 0 (where the flat tape is fixed) will have a zero in the "Station Distance", "Station Depth", and "Velocity" columns of the field form, since this station is landward (ideally outside the high water mark). Also note that Station 1 is located at the very edge of the stream channel (at the water's edge) and therefore will have negligible water depth and velocity. Therefore, water depth and velocity are assumed to be zero, and should be recorded as such in the "Station Depth" and "Velocity" columns of the field form. Record the "Station Distance" at Station 1 from the flat tape.

   Special consideration: if the edge(s) of the stream is a vertical abutment (e.g., bridge, pier, etc.), the "Station Distance" should be measured to the abutment, but the velocity should be measured next to or as close to the abutment as possible. As an alternative method, a "rule of thumb" is that the velocity can be estimated as 85 – 95% of the velocity at the adjacent station. If any of these conditions are encountered, record the observation in the field book and field form.

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7. For each "Station Number" in the field form, record the "Station Distance" from the flat tape and "Station Depth" from the meter rod. Depending on the flow depth and conditions, apply the appropriate velocity measurement method as discussed below. The methods should be considered in the order as listed below, with highest priority listed first.

    a. *Two-Point Method:* The two-point method should be considered the default method, and specifies velocity measurements at two depths below the surface that are equal to 0.2 * Station Depth (shallower) and 0.8 * Station Depth (deeper). The two velocities should be averaged to obtain the representative velocity at that observation vertical. Use the two-point method for measuring velocity if the depth is greater than 1.5 feet deep for the ADV meter (or 2.5 ft for mechanical current meter). To field test whether two-point velocity measurements are representative, compare the 0.2 velocity measurement to the 0.8 velocity measurement. The 0.2 velocity should be greater than the 0.8 velocity but less than twice the 0.8 velocity. If this is violated, then the Three-Point Depth or other measurement method should be used.

    Special consideration should be given for measurements made within 0.2 feet of the streambed, solid surface, or water surface for the ADV meter (or 0.4 ft for mechanical current meters), as flow may be underestimated due to these boundary interferences. If any of these conditions are encountered, please record in the field book.

    Special consideration should also be given if depths are too great for the meter rod (creating an unsafe condition to collect the 0.8 measurement), in the presence of surface debris or ice (resulting in non-representative flows at the 0.2 measurement), or when the stream is moving too swiftly or stage is changing too quickly (creating an unsafe situation and/or non-representative flow in the time required to collect two measurements). If any of these conditions are encountered they should be recorded in the field book, and the methods listed below should be considered instead.

    b. *Three-Point Depth Method:* The three-point method specifies velocity measurements at three depths below the surface that are equal to 0.2 * Station Depth (shallower), 0.6 * Station Depth (Intermediate), and 0.8 * Station Depth (deeper). This method combines the Two-Point and Six-Tenths Depth Methods. The mean velocity is obtained by averaging the 0.2 and 0.8 depth observations, and then averaging this result with the 0.6 depth measurement. This method is used when the velocities in the vertical profile are abnormally distributed. As with the Two-Point Method, the depth must exceed 1.5 feet for the ADV meter (or 2.5 ft for mechanical current meter) to use this method.

    c. *Six-Tenths Depth Method:* The six-tenths depth method specifies a velocity measurement at a depth below the surface that is equal to 0.6 * Station Depth. Use the six-tenths depth method if the depth is less than 1.5 feet for the ADV meter (or 2.5 ft for mechanical current meter). Also use this method if other conditions are present that prevent the use of the two-point method, such as surface debris or ice interfering with the 0.2 depth measurement, or if the stream is moving too swiftly or stage changing too quickly to collect both depth measurements.

    d. *Two-Tenths Depth Method:* The two-tenths depth method specifies a velocity measurement at a depth below the surface that is equal to 0.2 * Station Depth. This method is used mainly during periods of extremely high flow when the velocities are great, making it impossible to obtain reliable velocity measurements at the 0.6 or 0.8 depth. A multiplier of 0.87 is typically used as the multiplier for the velocity readings.

e. *Float (Surface) Method:* The float (or surface) method should be used when none of the methods listed above are appropriate. This method is appropriate during flood conditions when it is not possible to use a current meter due to excessive velocities and depths, or where velocities and depths are too low for a current meter measurement. This method involves timing a floating object over a known or estimated distance. The object must be visible from shore, buoyant, not affected by the wind, and naturally degrading. Examples are debris, ice blocks, pine cones, wood blocks/branches, and oranges.

Note that additional procedures are necessary with the float method that are not needed with the other methods listed above. A beginning and ending point need to be marked on the stream/channel bank (preferably with stakes/flags) that are at least 2 – 3 stream widths apart. If possible, the travel time should exceed 20 seconds. The cross-sectional stream/channel area should be recorded at the stop and start markers and then averaged to obtain the mean cross-sectional area. If only one cross-sectional area can be measured, choose the downstream (ending) marker section. Note that the method detailed earlier in this SOP (with respect to Figure 1) can be used to obtain depth and width readings.

The float object should be dropped into the stream/channel upstream of the beginning marker. The timer should be started when it crosses the beginning/start marker and stopped when it crosses the ending/stop marker (note that two observers work best, depending on the distance traveled and flow velocity). Velocity is calculated as distance divided by time (L/T). Repeat the procedure 5 – 10 times, tossing the float a different distance from the bank to obtain a rough average of velocities across the stream/channel width. The average velocity of the float attempts is then calculated.

Because surface velocities ($V_{surface}$) are typically higher than mean or average velocities (V_{mean}), a coefficient (k) is necessary to convert the surface velocity to the mean velocity in the vertical profile ($V_{mean} = k*V_{surface}$). These coefficients generally range from 0.84 to 0.90. The higher values are usually associated with smooth streambeds or artificial channels, and the lower values are associated with irregular streambeds. A coefficient of 0.85 is commonly used.

8. In order to determine the velocity at a point with a current meter, it is necessary to immerse the meter at that point for a measured interval of time, usually 40 to 70 seconds. When applicable or appropriate, velocity readings should be allowed to stabilize to within 10% of the previous reading. For example, record the reading “15 cfs” if subsequent reading is between “13.5 and 16.5 cfs;” otherwise, continue collecting readings. If the stage (i.e., depth) or velocity is rapidly changing during measurement, note this on the field form, and only permit enough time for the meter to stabilize such that safe conditions allow.

9. Once the Station Distance, Station Depth, and velocity(s) are recorded next to the appropriate Station Number, move to the next station and repeat this procedure until the water edge on the opposite stream bank is reached.

Stream Flow Rate - Calculations

Once field measurements are completed, total stream flow can be calculated. Regardless of the method used to determine flow velocity, stream flow is found using the equation: flow (Q) = cross sectional area (A) * mean velocity (V).

Total stream flow is found by calculating and then summing stream flow in the individual segments or sub-sections. Two methods can be used to calculate stream flow using the velocity-area concept: i) mean-section method, and ii) mid-section method. Figure 2 below shows the calculation differences between the

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two methods, both visually and in equation form. The mid-section method was also shown previously in Figure 1.

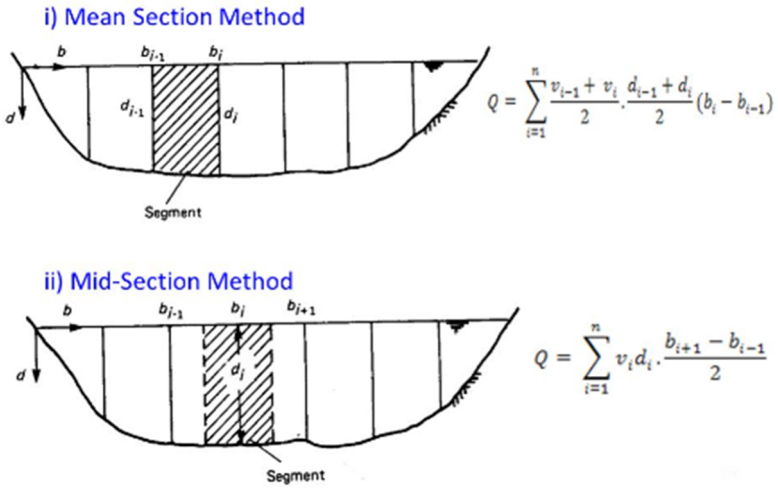


Figure 2 – Stream Flow Velocity-Area Calculation Methods

i) As the name suggests, the mean-section method uses the average velocity and depth across a segment. The segment is taken as the distance between successive observation verticals (the observation vertical is where the depth and velocity readings are taken).

ii) The mid-section method uses the actual depth and velocity recorded at the observation vertical (no averaging required), but then calculates the average segment width using the distance to the adjacent observation verticals. Also see equations in Figure 1, which provide further detail, particularly for calculations involving the stream edge observation verticals.

Either calculation method can be used, although the mid-section method is somewhat more rigorous and is the preferred method of USGS when using point velocity meters (Turnipseed, 2010). Calculations can be performed manually, or with the use of the spreadsheet associated with this SOP (SOP_#2101_Stream Flow_Site Selection Criteria & Measurement with V-A Method (2021).xlsx). Note that the spreadsheet contains a calculation page for velocity readings obtained by a current meter, as well as a page for velocity readings obtained by the Float (Surface) Method. The velocity readings obtained by a current meter are further broken down into flow rate calculations by either the mean-section or mid-section methods. The spreadsheet also contains field forms, which are included in Attachment 1 of this SOP.

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Attachment 1

Field Forms

STREAM FLOW MEASUREMENT FIELD FORM - CURRENT METER

Personnel: _____ **Date:** _____

Equipment: _____ **Gauge Reading Start:** _____

Location: _____ **Gauge Reading End:** _____

Weather: _____ **Average Gauge Height:** _____

Starting Point Facing Downstream (right or left): _____

Stream Conditions/Notes: _____

Station Number	Station Distance (from stake/Station 0) (ft)	Station Depth (ft)	0.6d Velocity (ft/s)	0.2d Velocity (ft/s)	0.8d Velocity (ft/s)	Notes
0 (at stake)	0.00	0.0				
1 (at water edge)						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						

STREAM FLOW MEASUREMENT FIELD FORM - FLOAT METHOD

Personnel: _____ **Date:** _____

Equipment: _____ **Gauge Reading Start:** _____

Location: _____ **Gauge Reading End:** _____

Weather: _____ **Average Gauge Height:** _____

Starting Point Facing Downstream (right or left): _____ **Float Type Used:** _____

Stream Conditions/Notes: _____

Float Run #	Run Distance (ft)	Run Time (s)	Notes	Float Run #	Run Distance (ft)	Run Time (s)	Notes
1				6			
2				7			
3				8			
4				9			
5				10			

(Upstream Cross-Section)				(Downstream Cross-Section)			
Station Number	**Station Distance (from stake / Station 0) (ft)**	**Station Depth (ft)**	**Notes**	**Station Number**	**Station Distance (from stake / Station 0) (ft)**	**Station Depth (ft)**	**Notes**
0 (at stake)	0.00	0.0		0 (at stake)			
1 (at water edge)				1 (at water edge)			
2				2			
3				3			
4				4			
5				5			
6				6			
7				7			
8				8			
9				9			
10				10			
11				11			
12				12			
13				13			
14				14			
15				15			
16				16			
17				17			
18				18			
19				19			
20				20			
21				21			
22				22			
23				23			
24				24			
25				25			

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Standard Operating Procedure

Stream Flow Measurement Using Flowtracker 2 ADV

Introduction

The purpose of this Standard Operating Procedures (SOP) is to define the methodology to be used for measuring stream flow in a wadeable stream using the SonTek FlowTracker2, an Acoustic Doppler Velocimeter (ADV).

Stream flow measurement with the FlowTracker2 unit incorporates the Velocity-Area Method of stream flow calculation. Foth SOP #2101 (Stream Flow Site Selection Criteria & Measurement with Velocity-Area Method) (Foth, 2021) addresses both the Velocity-Area Method and stream flow site selection criteria in detail, and should be referenced in conjunction with the use of the FlowTracker2 unit. This SOP covers only the use of the FlowTracker2 unit itself.

References

Foth, 2021. *Foth Standard Operating Procedure #2101*, Stream Flow Site Selection Criteria & Measurement with Velocity-Area Method.

SonTek, 2016. *FlowTracker2 User's Manual 1.1, Software Version 1.1, Firmware Version 1.17*. SonTek, San Diego, California. http://www.geotechenv.com/Manuals/SonTek_Manuals/sontek_flowtracker2_manual.pdf

Turnipseed, D.P., and Sauer, V.B., 2010. "Discharge Measurements at Gaging Stations," Techniques and Methods Chapter 8 of Book 3, Section A (3-8A), U.S. Geological Survey, Reston, VA. (Also available at *http://pubs.usgs.gov/tm/tm3-a8/*.)

Personnel Qualifications

A minimum of one qualified person is required to complete field measurements. A qualified person shall be someone who is formally trained in hydrology via an Accreditation Board for Engineering and Technology (ABET)-accredited engineering college or university and experienced in making open channel flow measurements. A qualified person may also be a technician lacking formal college training in hydrology but whom has been formally trained in open channel flow measurements using the procedures described in this SOP.

Personnel performing open-channel flow measurements shall have access to the project Health and Safety Plan (HASP). Note that the HASP may require a minimum of two people to be present when near water features such as rivers and streams.

Additional Health and Safety Training Recommendations:

- Field personnel shall have current CPR (Cardiopulmonary Resuscitation) and First Aid training.

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- Field personnel shall have satisfied Occupational Safety and Health Administration (OSHA) training requirements (40 CFR 1910.120) if hazardous materials are known to be or may be present at the site.

- Field personnel shall have satisfied Mine Safety and Health Administration (MSHA) safety training requirements prior to making open channel flow measurements on a project site regulated by MSHA.

Equipment and Supplies

- FlowTracker2 handheld unit and probe
- Top setting wading rod with attachment for FlowTracker2
- Measuring tape or graduated tag line
- Metal or wood stakes
- Hammer or fence-post driver
- Rake (optional)
- Field book
- Waterproof marker or pen
- 8 extra AA batteries
- Hip or chest waders
- USGS-approved personal flotation device
- Rain gear, if applicable

Procedures

1. Review the Health and Safety Plan (HASP), Work Plan, and manufacturer's instructions for operating the FlowTracker2.

2. Assemble inventory of materials, supplies, and equipment.

3. Prior to departing to the field site, perform the Office Diagnostic Procedure on the FlowTracker2 as described in Section 7.1.3 of the FlowTracker2 User's Manual. From the Utilities menu, manually check the battery life, clock, and GPS location. To verify Raw Data and Beam Check functions, place the FlowTracker2 probe in a bucket of water. Check the velocity, SNR, temperature, and tilt plots to ensure they conform to expected values as defined in the User's Manual. Execute the Automated Beam Check. The Automated Beam Check should complete successfully without error messages. It may be necessary to add a small amount of sediment to the water for the beam check to work properly. If the Beam Check generates errors, contact the manufacturer for resolution or servicing of the instrument.

4. The FlowTracker2 default setting is metric units. If U.S. Customary Units (USCS) are required, change the unit setting: from the main menu, select Device Configuration, then Application Settings. Set units to "English."

5. See Foth, 2021 for flow measurement site selection criteria. At the selected discharge measurement location, fix a measurement tape or tag line across the water at a height visible while wading in stream. The line must be graduated in units of length using a system of units consistent with those that will be recorded via the FlowTracker2. Secure the tape to stakes, competent trees, or another method that will provide a secure fixture for the tape. Do not fix lines across a stream if there is a risk of entanglement with water-craft users.

6. Assemble the FlowTracker2 and a top-setting wading rod and position the FlowTracker2 in the stream such that the blue arm that attaches the FlowTracker2 probe to the wading rod is pointing upstream and the wading rod is vertical (no tilt). Face upstream and position the FlowTracker2 upstream of the

operator. Measurements can be initiated from either the right bank or left bank. Maintain an upstream-facing position with the FlowTracker2 deployed upstream of the operator during all measurements.

7. Activate the FlowTracker2 to begin recording velocities/discharge. In the main FlowTracker2 menu, select "Measurement." On the next screen, "New File Type," select "Discharge." On the next screen, "New File Template," then select "Default". On the next screen, "New Data File," populate the site information. Press OK to continue.

8. The FlowTracker2 menu will then prompt you to make an automated Beam Check. With the FlowTracker2 probe submerged in moving water and well away from underwater obstacles, press "Start." Allow the beam calibration cycle to complete. If the Beam Check completes without errors, press "Done" and continue step 9. If the Beam Check does not complete without errors, repeat the Beam Check. Failure to submerge the probe in moving water may result in Beam Check errors. If repeated, Beam Check calibrations fail to complete free of errors, terminate the measurement effort and contact the manufacturer for service.

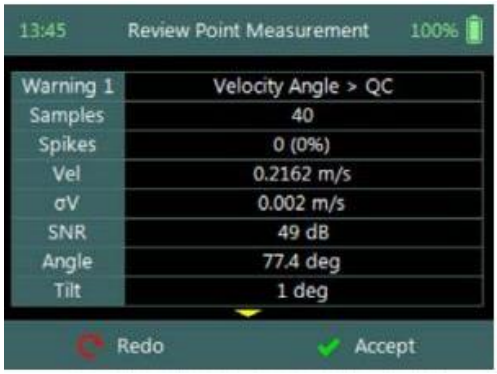
9. Make the first measurement at the bank. In the "Data Collection" screen, press "Add Station." Input distance reading from the tag line corresponding to the position of the wading/suspension rod ("Location") and water depth as indicated on the wading. Water depth should be entered to the maximum precision provided by the wading rod. A properly graduated wading rod must be used to obtain required accuracy. Using the drop down menu, define whether the first measurement is at the left or right bank (left or right bank definition is made by the user based upon a reference frame oriented downstream). Leave the "Correction Factor" on the default setting of 1. Select the "Velocity Method." The preferred option for the velocity method is the two point method in which measurements are made at depths below the water surface of 0.2 x full depth and 0.8 x full depth (0.2/0.8d). If the stream is less than 1.5 feet deep, select the 0.6-depth method to collect velocity measurements at only one depth (0.6 x full depth below the water surface) per station. See Foth, 2021 for a detailed description of various velocity-area methods (number and depths of measurements), depending on stream depth and flow conditions.

   Select "Measure." If using the 0.2/0.8d velocity method, the "Measurements" screen will appear and the user will be prompted to select the 0.2d measurement or the 0.8d measurement. Select the desired depth for the first measurement.

10. The display on the handheld unit will update and prompt the user to position the suspension rod such that the Vernier scale on the wading rod corresponds to the depth selected in the previous step. Adjust (raise or lower) the suspension rod according to the graphic display to position the probe to the appropriate depth. Press "Start" and hold the rod upright until the measurement is completed; the measurement-progress graphic display indicates the progress of the measurement and when it has been completed. If the green bubble indicator on the screen turns red, it is an indication of excessive tilt of the wading/suspension rod. If excessive tilt is indicated, reposition the rod to eliminate the warning and repeat the measurement.

11. Following completion of the measurement described in the previous step, the handheld unit will index to the next screen, "Review Point Measurement" (shown below). On this screen, review the measurement just completed. See pages 124-126 of the FlowTracker2 User's Manual for definitions of variables. Verify that the measured flow velocity is within the expected range based on historic measurements and observed conditions. If the measurement is acceptable, record the measurement data on the field form and select "Accept" using the FlowTracker2 user interface.

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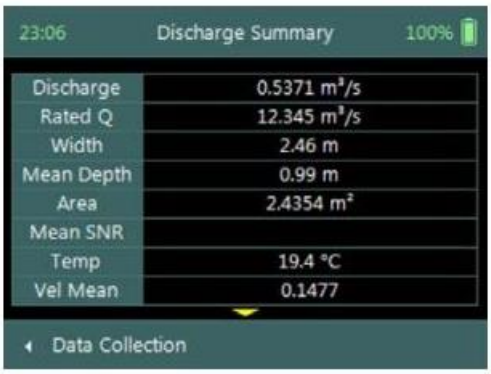
If the measurement is not acceptable, repeat the measurement (Step 10). Encountering a negative velocity is indicative of instrument error or a flow reversal. Observe the current in the stream. If a flow reversal is apparent or likely, consider selecting a different location free from eddies and flow reversals. If actual reversed flow is likely and an alternate section is not an option, turn the instrument to direct it downstream with the operator standing upstream and slightly to the side. Observe the indicated velocity. If the velocity observed in this reversed orientation is similar to the absolute value of the negative velocity observed during normal (upstream) orientation, turn around to face in the upstream direction and reposition the probe and wading rod in the same location as that occupied when the original negative velocity was observed. Complete the measurement as normal and "Accept" and record the negative velocity. Reduce the width of station sections until positive velocities are observed and continue making measurements.

When calculating total discharge, check calculations to ensure that the negative velocity stations are treated as negative flow. If using a multi-point method per station, such as the two-point method (0.2 & 0.8 depths), the user will be prompted via the "Measurements" screen to setup for the next measurement at the current station. Select the desired measurement. Repeat steps 10 and 11 for the remaining measurements at the current station.

12. Move the probe to the next station. As a general rule, the distance between stations should be such that 10% or less of the total discharge passes through each station section. Generally, station widths tend to be in the 1 – 3 foot range. In those portions of the stream section characterized by higher velocity, station section width should be reduced by using smaller horizontal offsets between each measurement. See Foth, 2021 for a more detailed description of station width determination. Repeat steps 9-11. On the "Add Station" screen, select "Station Type Open Water."

13. When velocity/discharge measurements have been completed at each station across the stream section, including the Left Bank and Right Bank measurements, view the discharge summary from the "Data Collection" menu and record the total discharge on the Field Form.

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Review individual station data and the total discharge result and compare to historic results and observed site conditions. Determine if any results depart widely from past results or observed conditions.

If an erroneous measurement is suspected, delete the station and collect a new measurement at or near the previous measurement location. Also, if one or more stations recorded more than 5% of the total discharge, further subdivide the stream section at that station by making additional station measurements (using the same vertical discretization as used in the suspect stations) to either side of the original measurement location.

14. When measurement is complete, select "Complete Measurement" from the "Data Collection" menu. Select "OK," then "Complete." This will close the measurement file and the user will not be able to add additional stations or make any changes to the data. From the Summary page, copy the final discharge onto the field form.

15. Download FlowTracker2 software to a laptop or desktop computer from the flash drive provided with the FlowTracker2. See pages 206-207 of the FlowTracker2 User's Manual for directions to install and navigate the software.

16. Open the FlowTracker2 program on the computer. Connect the FlowTracker2 handheld unit to the computer using the USB to micro USB cord included with the FlowTracker2. The measurement probe does not have to be connected to the handheld unit during this process. Turn on the FlowTracker2. From the main menu, select "Communication." On the computer, select the "Device" icon in the upper left corner of the FlowTracker2 user interface, then select "USB." Files stored in the FlowTracker2 handheld unit will display in a list. Highlight the desired files and select "Export" in the upper left corner of the screen. Select a location to save on the computer hard drive. Locate the files on the computer and email them to the Foth Project Discipline Leader or Project Manager.

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Standard Operating Procedure

Stream Flow Measurement Using ADCP

Introduction

The purpose of this Standard Operating Procedures (SOP) is to establish a standard procedure for calculation of streamflow measurements in open channels using an Acoustic Doppler Current Profiler (ADCP). This procedure provides a basic introduction to ADCP methodology with a detailed description of methods for using the Sontek RiverSurveyor M9 or S5 ADCP.

This procedure can be adapted for use with other brands of ADCPs by following the quality guidelines outlined in this document and the instrument-specific instructions included with a particular ADCP. This procedure is applicable to streamflow measurements made via taglines during open channel flow conditions.

Stream flow measurement with ADCP units incorporates the Velocity-Area Method of stream flow calculation. Foth SOP #2101 (Stream Flow Site Selection Criteria & Measurement with Velocity-Area Method) (Foth, 2021) addresses both the Velocity-Area Method and stream flow site selection criteria in detail, and should be referenced in conjunction with the use of the ADCP units. This SOP covers only the use of the Sontek RiverSurveyor M9 unit itself.

References

ASTM Standard D5089-95, 2014. "Standard Test Method for Velocity Measurements of Water in Open Channels with Electromagnetic Current Meters," ASTM International, West Conshohocken, PA, 2014, DOI: 10.1520/D5089-95R14, www.astm.org.

Australian Government Bureau of Meteorology (AGBM), 2013. "National Industry Guidelines for Hydrometric Monitoring Part 8: Application of Acoustic Doppler Current Profilers to Measure Discharge in Open Channels," Water Information Standards Business Form 100.08-2013. http://www.bom.gov.au/water/standards/niGuidelinesHyd.shtml.

Foth, 2021. *Foth Standard Operating Procedure #2101*, Stream Flow Site Selection Criteria & Measurement with Velocity-Area Method.

New Zealand National Environmental Monitoring Standards, 2013. "Open Channel Flow Measurement: Measurement, Processing, and Archiving of Open Channel Flow Data," Version 1.1. http://www.lawa.org.nz/media/16578/nems-open-channel-flow-measurement-2013-06.pdf

SonTek, 2014. "RiverSurveyor S5/M9 System Manual Firmware Version 3.50," SonTek, San Diego, CA.

Turnipseed, D.P., and Sauer, V.B., 2010. "Discharge Measurements at Gaging Stations," Techniques and Methods Chapter 8 of Book 3, Section A (3-8A), U.S. Geological Survey, Reston, VA. (Also available at *http://pubs.usgs.gov/tm/tm3-a8/*.)

U.S. Geological Survey, 2013. "Measuring Discharge with Acoustic Doppler Current Profilers from a Moving Boat," Chapter 22 of Book 3, Section A, Techniques and Methods 3-A22, U.S. Geological Survey, Reston, VA, http://www.lawa.org.nz/media/16578/nems-open-channel-flow-measurement-2013-06.pdf

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Personnel Qualifications

A minimum of one qualified person is required to complete field measurements. A qualified person shall be someone who is formally trained in hydrology via an Accreditation Board for Engineering and Technology (ABET)-accredited engineering college or university and experienced in making open channel flow measurements. A qualified person may also be a technician lacking formal college training in hydrology but whom has been formally trained in open channel flow measurements using the procedures described in this SOP.

Personnel performing open-channel flow measurements shall have access to the project Health and Safety Plan (HASP). Note that the HASP may require a minimum of two people to be present when near water features such as rivers and streams.

Additional Health and Safety Training Recommendations:

- Field personnel shall have current CPR (Cardiopulmonary Resuscitation) and First Aid training.
- Field personnel shall have satisfied Occupational Safety and Health Administration (OSHA) training requirements (40 CFR 1910.120) if hazardous materials are known to be or may be present at the site.
- Field personnel shall have satisfied Mine Safety and Health Administration (MSHA) safety training requirements prior to making open channel flow measurements on a project site regulated by MSHA.

Equipment and Supplies

Required equipment will vary according to the site conditions and may include the following:

- Tape measure
- ADCP and all accessory cables, batteries, etc.
- Hydroboard
- Buoys or other markers for section edges
- Laptop with appropriate software (RiverSurveyor Live for RiverSurveyor M9/S5)
- Tagline (longer than the stream width)
- 2 ropes for pulling the ADCP across the river (longer than the stream width)
- Waterproof marker or pen
- Field Log Book
- Hip or chest waders
- USGS-approved personal flotation device
- Rain gear, if applicable
- Stakes to secure tagline
- Boat, if needed to set up tagline

General Measurement Theory and Considerations

ADCP instruments estimate discharge from measurements of water velocity, water depths, and instrument velocity. Measurements are made with an acoustic pulse of a known frequency coupled with measurement of the “Doppler shift” in the returned signal from reflective particles in the water (AGBM, 2013). The depth to streambed is also measured using reflected sound waves (USGS, 2013). Instrument velocity is determined from bottom tracking or using a GPS.

Measurement depth capabilities of ADCPs vary and the devices are commonly used in streams that are too deep to measure flow with a flow meter on a wading rod. ADCPs cannot measure water

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velocities along the stream surface, stream bottom, and edges, and must compute an estimated flow in these areas. Therefore, ADCPs require a minimum depth of water to compute quality streamflow data where the majority of flow does not occur in these estimated flow zones. The following factors affect the overall quality of a discharge measurement (USGS, 2013 and AGBM, 2013):

- Proper site selection
- Maintaining slow, steady instrument speed
- Inadequate sediment in the water (not enough signal reflected)
- Excessive sediment in the water (excessive attenuation of signal)
- A moving bed load (reduces bottom tracking accuracy)
- Instrument capabilities
  - The depth range of a RiverSurveyor M9 is 1 ft – 131 ft
  - Maximum recordable water velocity of a RiverSurveyor M9 is 66 ft/s
  - Minimum water velocity of a RiverSurveyor M9 is 0.3 ft/s
- Operator error
  - Reduced by following the guidelines in this SOP

Of these factors**, instrument speed and site selection have been identified as the two most important influences on data quality**. The following procedure provides for the safe collection of quality streamflow data using an ADCP.

Procedures

Step 1: Office Preparation Prior to Sampling

1. Review all company health and safety procedures and the QAPP with all field personnel.

2. Check current weather conditions. Stream gauging may be hazardous during extreme weather. Storm events can lead to rapidly changing stream flows and reduce consistency between transects.

3. Check the ADCP for signs of wear and verify that all components are present including (Figure 1):

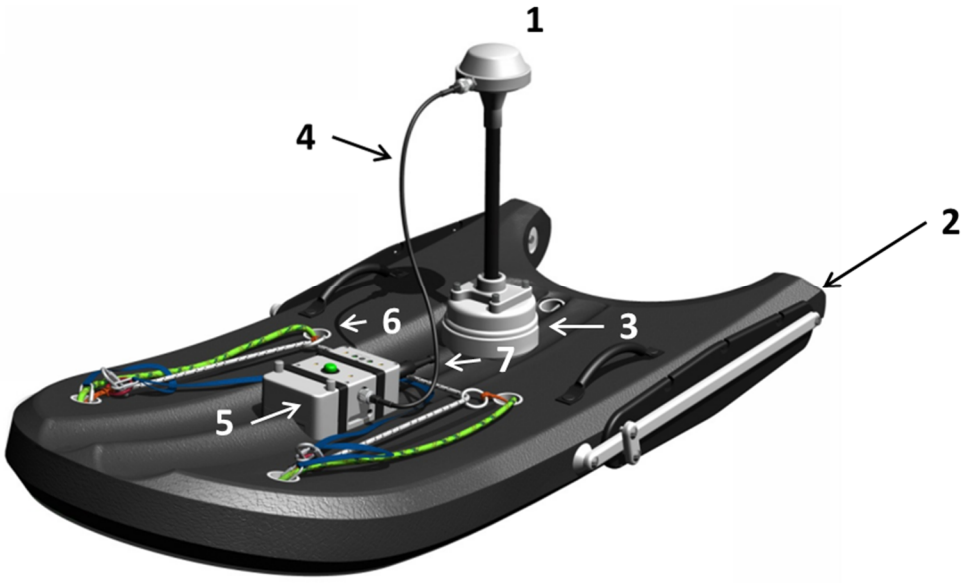


Figure 1. Basic RiverSurveyor setup, adapted from Sontek (2014).

1. **GPS Antenna**
2. **Hydroboard**
3. **ADCP**
4. **Cable connecting the GPS antenna to the PCM**
5. **Power and communications module (PCM)**
6. **Cable connected the ADCP to the PCM**
7. **Bluetooth antenna to transmit data to the computer**
8. **Laptop with Bluetooth dongle to receive data transmissions from the ADCP (not shown)**

4. Check that the system is working and the Bluetooth communication is configured correctly.
    a. Put the battery packs into the PCM, connect the ADCP, and attach the Bluetooth antenna.
    b. Plug in the Bluetooth dongle to the computer.
    c. Start RiverSurveyor Live and click "Connect to a RiverSurveyor System" from the main screen shown in Figure 2.
    d. The program may automatically detect the ADAP and a pop-up window will ask to connect to the detected system.
    e. Note: a GPS error may pop up if the system check is done inside where satellite reception is poor. Ignore this error; this check is to see if the ADCP system can be detected and the Bluetooth communication is functioning.

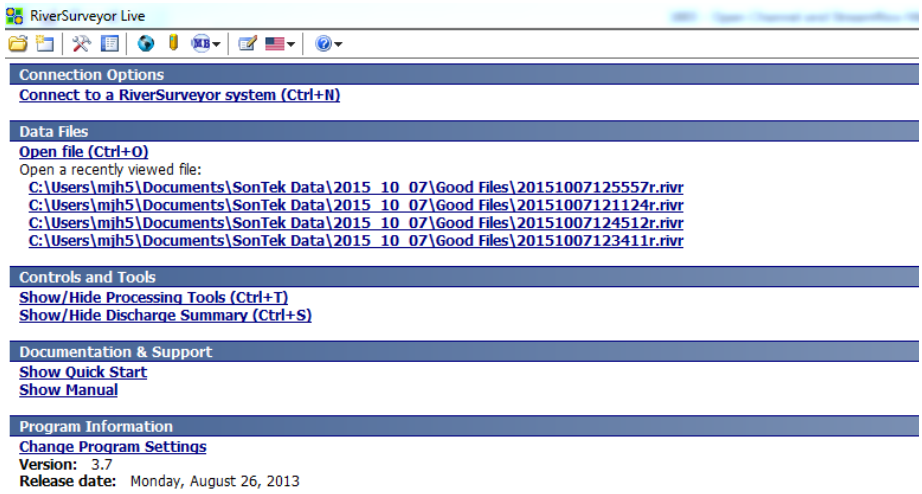


Figure 2. Main screen of the RiverSurveyor Live software program.

5. Remove battery packs (do NOT store unit with batteries inside the PCM). Re-store the ADCP in the provided case for transport.
6. Collect remaining field gear.
7. Check that the laptop is fully charged.
8. Check and **RECORD** the magnetic declination using: http://www.ngdc.noaa.gov/geomag-web/#declination

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Step 2: Selecting a Site

Proper site selection is one of the most important steps in collecting high quality streamflow data. Site selection for a streamflow measurement transect should follow the same guidelines used in selecting sites for velocity measurements with current meters, as outlined in ASTM Standard D5089-95 and in USGS (2013), and as summarized in Foth, 2021. Additionally, Turnipseed, 2010, contains site selection criteria specific to ADCP units. An abbreviated list of the site selection criteria found in these documents is as follows:

1. Stream section is straight with uniform, parallel flow.
2. Flow is free of eddies, slack water, and excessive turbulence.
3. Streambed is uniform and roughly parabolic, trapezoidal, or rectangular in shape.
    a. Avoid asymmetric geometries and channels with abrupt changes in streambed slope across the transect.
4. Streambed should be free of large boulders or excessive vegetation, if possible.
5. Water depth should be greater than two depth cells (depth cell dimensions depends on instrument type and measurement configurations) across >95% of the transect and generally exceed one foot.
6. Visually assess that the majority of streamflow is not moving along the stream edges.
    a. Velocity along the edges should be estimated when selecting a transect location prior to deploying the ADCP; there is less error associated with the overall discharge estimate if <5% of the total discharge is computed in the edge sections.
7. Water velocity should EXCEED 0.3 ft/s across much of the cross-sections. Velocities less than 0.3 ft/s can make it difficult to smoothly move the ADCP across the channel.
8. Avoid locations next to large metal objects, such as metal bridges which have local magnetic fields and can result in errors in the ADCP headings.

Step 3: Setting Up a Tagline and Edge Markers

A tagline is a line set up perpendicular to streamflow from which the ADCP and hydroboard will be tethered via a carabineer. Figure 3 shows an example of a tagline from USGS (2013). The line should be a couple of feet above the water surface so that the Hydroboard with the ADCP rides flat in the water. The tagline should be secured to the stream bank using stakes or available site anchors, such as trees. A boat may be necessary to set up the tagline. Personal floatation devices should always be worn when in the boat or working near the river.



Figure 3. Tagline example, from USGS (2013).

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A tagline is the most reliable option for ADCP operation but at some sites, such as those with heavy boat traffic or at very wide rivers, setting a tagline may be problematic or unsafe. At these sites, the ADCP can be operated off the side of a boat using a rigid mount or by towing a tethered ADCP mounted on a Hydroboard. Potential complications from a manned boat include magnetic interference from the boat, water turbulence from the boat motor, and maintaining a straight transect. Instructions and additional considerations for discharge measurements from a manned boat are provided in Step 5b.

Edge markers (sticks or buoys) should be set up to mark the ending/starting edge on each side of the stream (Figure 4). During sampling, the ADCP transect terminates at these edge markers. The markers should be placed near the stream edge where the water depth becomes <1 ft for all streams with gently sloping edges. In streams with very steep, near-vertical banks, the ending/starting edge should be at a distance from the bank that equals the water depth (i.e., if the water depth is 10 ft adjacent to the stream edge then the ending/starting edge should be 10 ft from the bank).

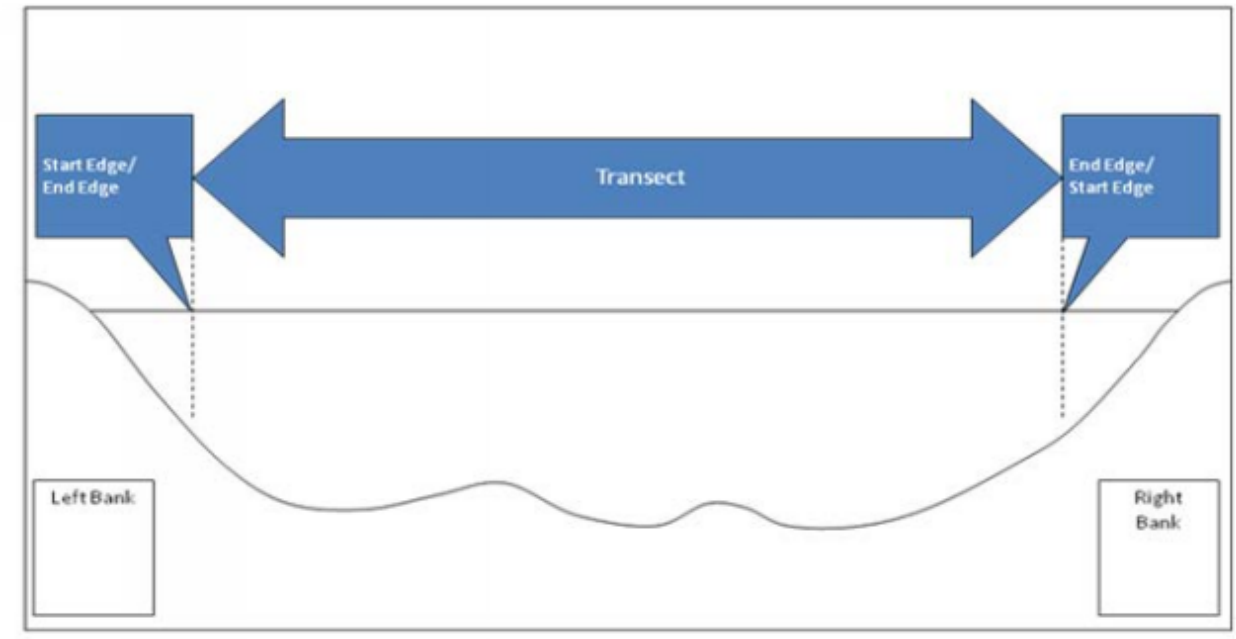


Figure 4. Example cross-section (looking downstream) showing the ending edges. The ADCP moves across the "Transect" portion of the cross-section and markers are placed at the starting/ending edges.

1. **RECORD** the distance from the stream bank to the ending/starting edge marker for both the left and the right banks. Also **RECORD** the water depth at each edge marker.
    a. *Note: The left and right banks are assigned looking DOWNSTREAM. When facing downstream the left bank is on the left side. Failure to assign the correct bank will result in a negative discharge.*
    b. It is important to accurately measure the distance from the edge marker to the stream bank because this value is used to estimate the flow along the stream edges. Poor quality estimates of this distance will increase uncertainty in the streamflow estimate.

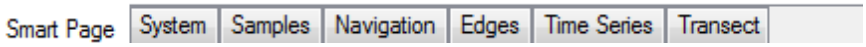
Step 4: Programming the ADCP

1. Assemble the ADCP, as shown in Figure 1. Mount the ADCP on the hydroboard and make sure that the sensor extends approximately two inches below the bottom of the board. Turn on the laptop and

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connect to the ADCP. The GPS light on the PCM should be green. The laptop should recognize the ADCP.

2. Select the "Smart Page" tab from the ribbon on the bottom left of the screen, shown below.



3. Follow the Smart Page (Figure 5) steps from top to bottom.

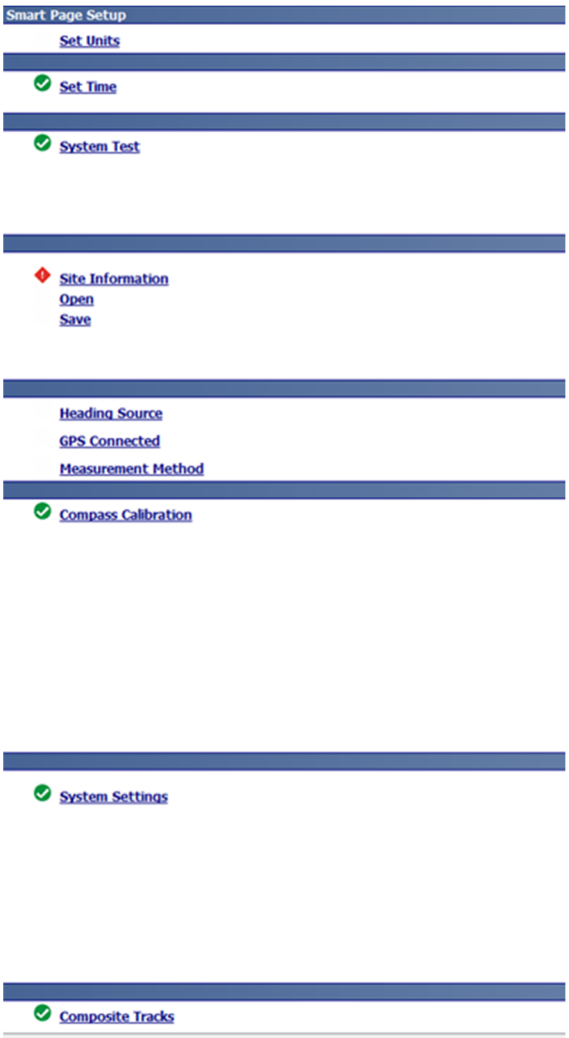


Figure 5. Screenshot of the Smart Page steps.

a. Click "Set Units" and select "English."
b. Click "Set Time" and sync to the computer's clock.
c. Click "System Test". This is a 60 second test to verify all hardware is functional. This test should be done every time the unit is set up at a new site.
    i. A "Pass" message should be displayed. If errors are displayed consult the user manual, call the rental company, or call the Foth contact. Do not attempt to measure flow if the system test fails.
d. Click "Site Information" and enter site details in the "Site Information" box (Figure 6).

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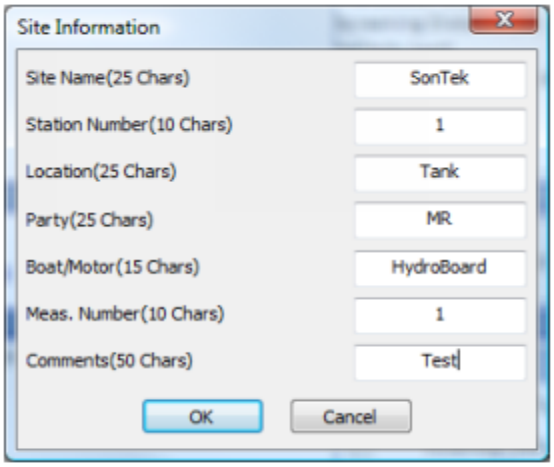


Figure 6. Screenshot of the Site Information box, from SonTek (2014).

i. Enter the location under "Site Name."
ii. "Station number" is "1."
iii. "Location" is optional if additional descriptors are necessary.
iv. "Party" should have the initials of the operator(s) collecting the measurements.
v. "Boat/Motor" should read "Hydroboard."
vi. "Measurement Number" should be updated if transects sets are collected.
vii. Enter "comments" if needed.

e. Click "Compass Calibration" and complete the compass calibration, as directed in the calibration window.
   i. Complete two horizontal rotations with pitch/roll values equal to or greater than expected measurement conditions. The required duration of the compass calibration is between 1 and 2 minutes.
   ii. The ADCP should be mounted on the hydroboard during the compass calibration. The operator should hold the hydroboard and spin in slow circles while walking around in a larger, 3-4 ft wide circle. During this time the pitch and roll should also be varied.
   iii. The instrument program will inform the user of a successful compass calibration. If the calibration is not successful, repeat until a successful calibration result is displayed by the computer.
f. Select "System Settings" and fill in the information shown in Figure 7.

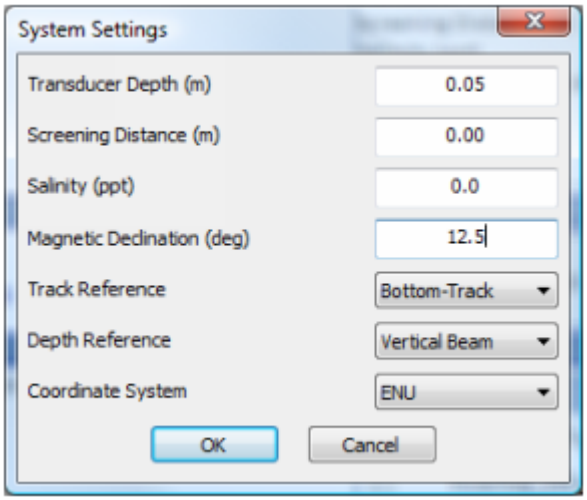


Figure 7. Screenshot of the System Settings box, from SonTek (2014).

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i. Enter the transducer depth, measured as the distance from the water surface to the middle sensor (bottom of the ADCP) when the hydroboard is sitting in the water, as shown in Figure 8.

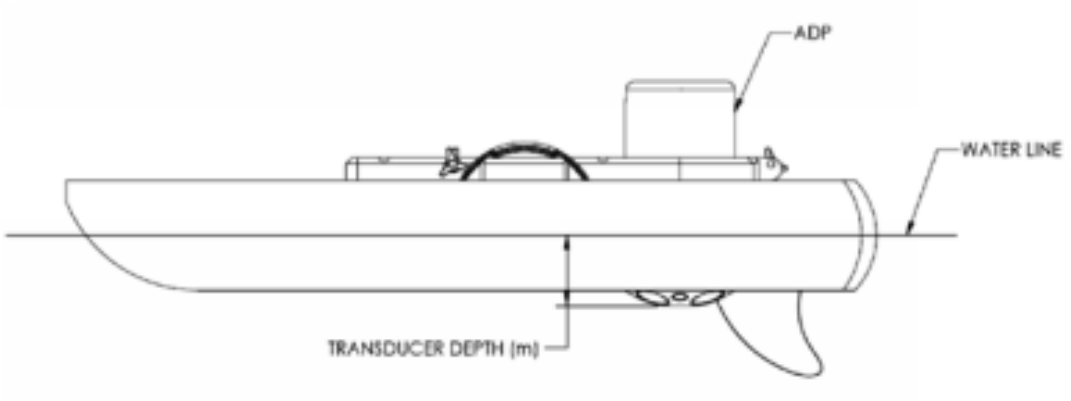


Figure 8. Measurement of sensor depth, from SonTek (2014).

ii. Leave the screening distance as 0.00 ft/m and the salinity as 0.0 ppt.
iii. Enter the appropriate magnetic delineation for the site in degrees with west as negative and east as positive. Magnetic declination can be found online or on USGS topographic maps.
    1. Source: http://www.ngdc.noaa.gov/geomag-web/#declination
    2. *Declinations change with time and should be calculated prior to each field visit.*
iv. Leave the track reference as "Bottom-Track", the depth reference as "vertical beam", and the coordinate system as "ENU".

g. Leave "Composite Tracks" as "Enabled".
h. Select "Edge Settings" and enter the distances to the right and left edges (recorded in Step 3). **RECORD** these distances.
i. Leave the default values in the "Profile Extrapolation Settings".
j. Position ADCP at the starting edge location and clip to the tagline (if used). Attach the two tether lines to the ADCP raft and have one person on each bank holding a line (if tagline is used). The instrument is now ready to make measurements.

Step 5a: Making a Measurement with the ADCP on a Tagline or by Remote Control

1. Once the ADCP is in position and both tether line handlers are ready, select "Start Measurement" from the left side of the screen in the "Smart Page" tab (Figure 9). No data are being recorded until "Start Edge" is selected.

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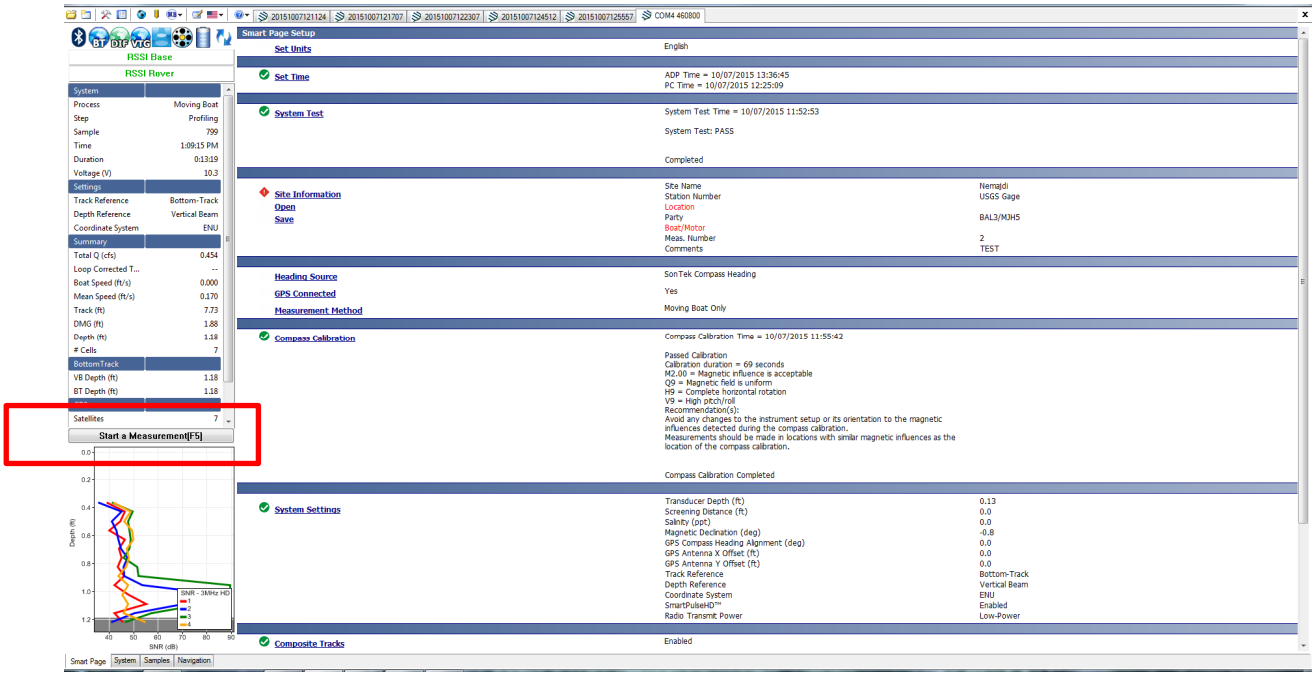


Figure 9. Screenshot of the start measurement screen.

a. Do not stand in the water near the ADCP while the meter is collecting data. Make all manual measurements required to program and operate the ADCP prior starting the flow measurement.

2. Select “Start Edge” from the left side of the screen and enter the edge data including if the transect is starting from the left or right bank and the distance from the bank to the starting edge (from Step 3) in the box shown in Figure 10. Retain the default values for Gauge Height and estimated flow. The ADCP is now collecting data. Maintain the starting position of the ADCP for 10 seconds (10 measurements) by keeping tension on both tether lines.

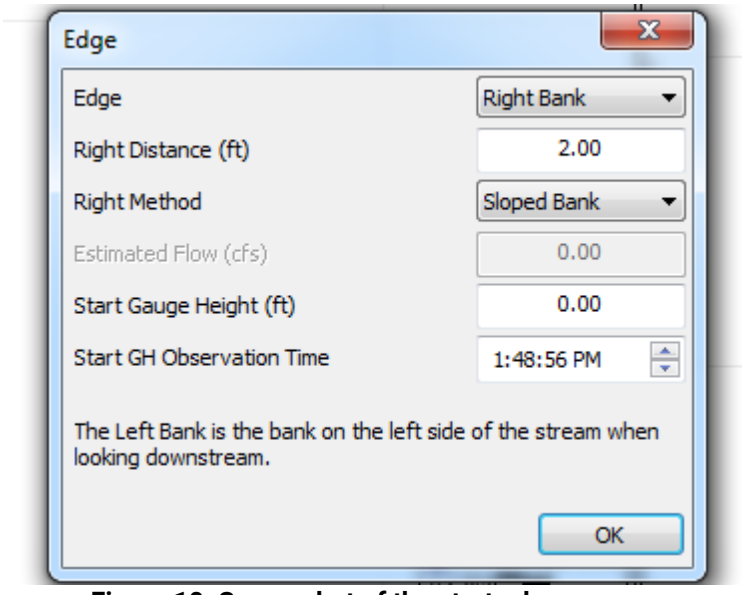


Figure 10. Screenshot of the start edge screen.

3. After collecting 10 measurements at the edge, select “Start Moving”, as shown in Figure 11. During operation of the ADCP, adhere to the following operating procedures and guidelines:

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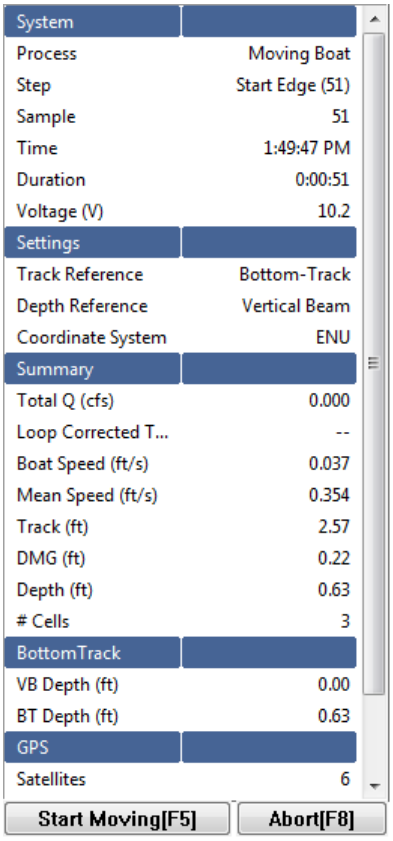


Figure 11. Screenshot of the start moving screen.

a. A minimum of two depth cells should be recorded at the edge. The number of cells can be viewed in at the bottom of the "Summary" section in the display, as shown in Figure 11.
b. Maintain a steady speed across the transect.
c. Instrument speed (boat speed) should be less than the water velocity. These values can be viewed in real time using the computer display shown in Figure 11.
d. A minimum of four passes along the transect should be collected with a total sample time of 720 seconds (12 minutes); each transect should take ~3 minutes or more. In cases of uncertainty, operate the unit to produce longer rather than shorter sample times for each pass.
    i. Maintaining a slow hydroboard speed (boat speed) and a steady movement increases measurement quality.
    ii. If the water velocity is very slow it may be necessary to move faster than the water velocity in order to maintain steady movement. If this is the case, more than 4 transects may need to be measured in order to sample for a total of 12 minutes.
        1. Always make transect measurements in pairs going both directions across the stream; if an additional measurement is needed, conduct an additional set of paired measurements (one pass in each direction).

4. Once the ADCP reaches the ending edge marker, select "End Transect" from the left menu and enter the edge data. Hold the instrument steady for 10 stationary measurements at the edge marker. After the 10 measurements are collected, select "End Transect" from the left menu.
5. Note, the system continues to collect data even after "End Transect" is selected. Until a total of 4 transects have been completed, a new transect should be started immediately by selecting "Start Edge" and then moving through the measurement steps again.
    a. There is no need to stop or pause between measurement passes across the stream transect.
6. Once 4 measurement passes across the transect have been collected select "End Transect" and then

"Abort" after the last ending edge data have been collected.

   a. Note: An equal number of measurement passes should be completed in each direction (from left bank to right bank and right bank to left bank) to remove directional bias from the data.

7. If a disruption occurs while collecting data, finish the measurement pass, and then collect an additional two measurement passes (one in each direction).

Step 5b: Making a Measurement with the ADCP from a Manned Boat

1. Set up edge markers as specified in Step 3. In addition to marking the starting and ending edges of the transect, edge markers will serve as guides for maintaining a measurement transect that is perpendicular to streamflow.
2. Program the ADCP following the directions in Step 4. Note that the ADCP is being operated from a manned boat in the comments section of the "Site Information".
3. Follow the operation instructions in Step 5a with the following exceptions:
   a. Instead of pulling the ADCP across the river, the ACDP will be mounted to the manned boat or on a Hydroboard tethered to the manned boat.
   b. The manned boat should be maneuvered in a straight, steady transect across the river.
   c. To avoid recording turbulence from the boat motor, the ADCP should be placed as far away from the motor as possible.

Step 6: Reviewing ADCP Data

1. Once four measurement passes along the transect have been completed and the data collection has been stopped by selecting "Abort", select the "System" tab from the bottom screen and download the transect files to a designated folder named by the site name and date of data collected. Figure 12 shows the download screen.
   a. Note, the system tab will not have a data download option if the instrument is still collecting data and the user did not select "Abort." The ADCP is not collecting data when the left system summary displays "Start a Measurement", as shown in Figure 12.

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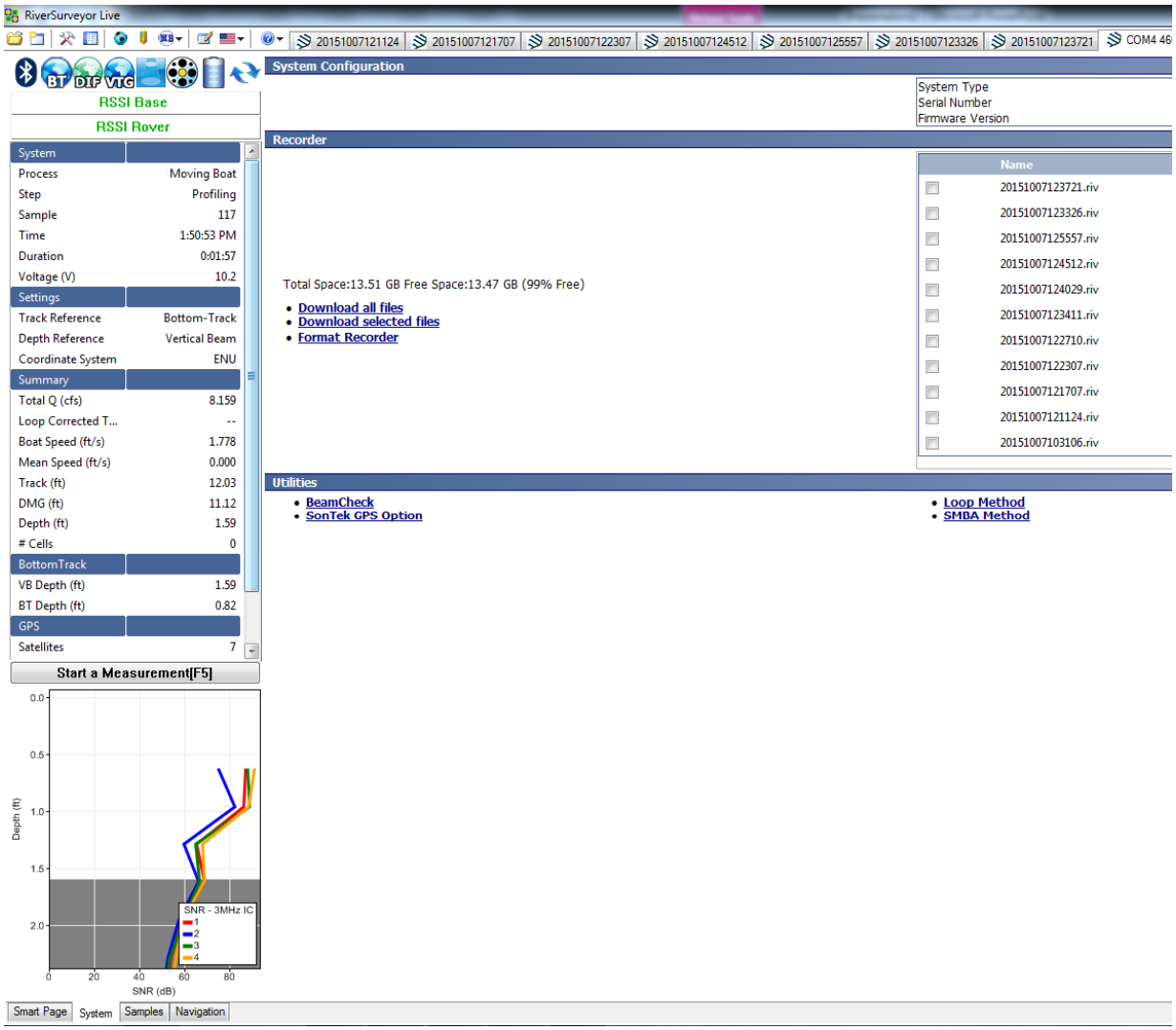


Figure 12. Screenshot of the data download screen.

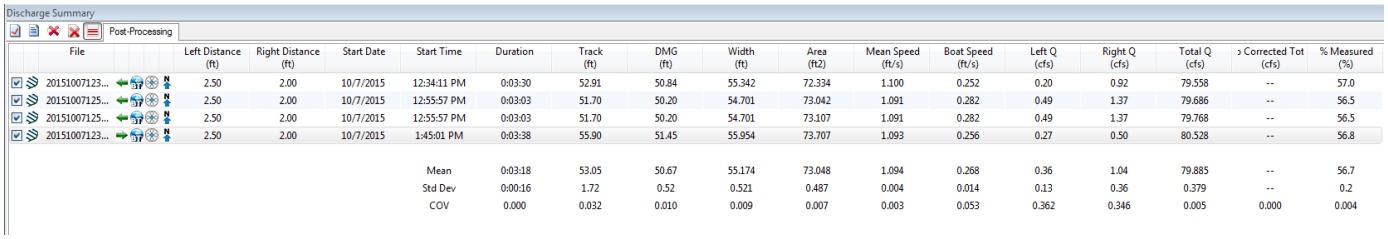
2. After data are downloaded, select the white and blue box icon for "Show/Hide Discharge Summary" from the top of the River Surveyor Screen, as shown in Figure 13.



Figure 13. Screenshot showing the discharge summary icon.

3. In the discharge summary report (Figure 14) make sure all four of the transects are selected.

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Discharge Summary

Post-Processing

File	Left Distance (ft)	Right Distance (ft)	Start Date	Start Time	Duration	Track (ft)	DMG (ft)	Width (ft)	Area (ft2)	Mean Speed (ft/s)	Boat Speed (ft/s)	Left Q (cfs)	Right Q (cfs)	Total Q (cfs)	Corrected Tot (cfs)	% Measured (%)
20151007123...	2.50	2.00	10/7/2015	12:34:11 PM	0:03:30	52.91	50.84	55.342	72.334	1.100	0.252	0.20	0.92	79.558	--	57.0
20151007125...	2.50	2.00	10/7/2015	12:55:57 PM	0:03:03	51.70	50.20	54.701	73.042	1.091	0.282	0.49	1.37	79.686	--	56.5
20151007125...	2.50	2.00	10/7/2015	12:55:57 PM	0:03:03	51.70	50.20	54.701	73.107	1.091	0.282	0.49	1.37	79.768	--	56.5
20151007123...	2.50	2.00	10/7/2015	1:45:01 PM	0:03:38	55.90	51.45	55.954	73.707	1.093	0.256	0.27	0.50	80.528	--	56.8
				Mean	0:03:18	53.05	50.67	55.174	73.048	1.094	0.268	0.36	1.04	79.885	--	56.7
				Std Dev	0:00:16	1.72	0.52	0.521	0.487	0.004	0.014	0.13	0.36	0.379	--	0.2
				COV	0.000	0.032	0.010	0.009	0.007	0.003	0.053	0.362	0.346	0.005	0.000	0.004

Figure 14. Screenshot showing the discharge summary report.

   a. If one measurement pass was bad, simply uncheck the box next to that measurement file to remove it from the discharge summary calculations. If a measurement pass is removed, make sure that the remaining measurements are paired measurement passes.

4. At the bottom of the discharge summary there is a mean Total Q (discharge) and a standard deviation. **RECORD** these two values in the field notebook.
   a. *The standard deviation should be less than 5% of the mean discharge. If this is not the case, two additional transects should be collected and then the discharge summary re-evaluated.*
      i. If there are outlying discharge measurements they may be discarded if additional transects are collected and provide consistent data.
      ii. If the flow measurements do not meet the 5% quality criteria call the Foth Technical Expert to discuss a path forward BEFORE leaving the field.
   b. **RECORD** the four discharge (Q) values used to compute the average flow.
5. The furthest right column of the discharge summary shows the "% Measured" flow. This is the amount of flow calculated by the measured velocities. Flow estimates are made at the stream surface, stream bottom, and at the edges. The percent flow measured should be greater than 40%, at a minimum, and ideally greater than 65% (NEMS, 2013).
   a. **RECORD** the mean "% Measured," found at the bottom of the summary report.
6. The data cross-sections for each measurement pass should be visually checked in the "Transect" tab.
   a. There shouldn't be any velocity spikes (rapid changes in velocity) in adjacent cells.
   b. Data gaps should be absent or minimal.
   c. The stream bottom should be smooth and free of sudden drops or spikes in the streambed elevation.
7. The flow measurement is now complete. Pack up all equipment. Disassemble the flow meter during transport.

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Streamflow Monitoring Field Form

Site ID:	Coordinate System and Units:
Date:	X-Easting :
Technician(s) Initials:	Y-Northing :

1. FIELD PARAMETERS

2.

pH (SU)	Specific Conductance (uMhos/cm)	Temperature (°C)	Dissolved Oxygen (mg/l)	Redox Potential (mV)	Turbidity (NTU)

ADCP MEASUREMENTS

Step 1: Office Preparation

Magnetic Declination:_____

Step 2: Site Selection

Transect is (circle answers, explain if NO is selected):

1. Straight with uniform flow? YES NO
2. Free of eddies, slack water and excessive turbulence? YES NO
3. Streambed is uniform and there are no abrupt changes in channel slope? YES NO
4. Water depth exceeds 1 ft across most of the transect? YES NO
5. Area is free of large metal objects? YES NO

Explanation (if any NOs were selected):

Step 3: Site Selection

Distance to Right Bank from Edge Marker:_____Units:_____

Distance to Left Bank from Edge Marker:_____Units:_____

Note: Banks are assigned looking downstream.

Step 4: Programming the ADCP

System Test Passed? YES NO

Compass Calibration Passed? YES NO

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Step 5: Making a Measurement

Collected at least 10 measurements at each edge marker? YES NO

Boat speed was less than water velocity? YES NO

Took at least 720 seconds (12 minutes) to complete the four transects? YES NO

Step 6: Reviewing the ADCP Data

Data files have been downloaded and saved in a folder? YES NO

Discharge Estimate 1: _____Units: _____

Discharge Estimate 2: _____Units: _____

Discharge Estimate 3: _____Units: _____

Discharge Estimate 4: _____Units: _____

Mean Discharge (from summary report):_____ Units: _____

Standard Deviation (from summary report):_____

Average % Flow Measured (from summary report):_____

Calculate 5% of the Mean Discharge (0.05 x mean discharge recorded above):

0.05 x _____ = _____

(Mean Discharge) (5% of the Mean Discharge)

Quality Checks

Is the standard deviation < 5% of the Mean Discharge? YES NO

Is average percent flow measured >40%? YES NO

If yes to both quality checks, measurement is complete. If no to either, call Foth contact to discuss.

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Standard Operating Procedure

Stage-Discharge Relation for Open Channel Flow

Introduction

The purpose of this Standard Operating Procedures (SOP) is to establish a standard procedure for development of a curve relating stage (elevation) to discharge. The SOP describes how discharge and stage data (obtained using methods covered in other Foth SOPs referenced herein) are used to create a relationship curve either manually or through computer programs. The curve can then be used to estimate discharge from future staff gauge measurements or in relation to a hydraulic control feature. This SOP applies to only to simple, freely-flowing, open-channel flow conditions, where channel hydraulics permit a stable relation between stage and discharge.

Please refer to the appropriate Foth SOPs for monitoring stream flow by other methods (e.g. velocity-area method, culvert flow, etc.) as well as for staff gauge installation and water level recording.

References

ASTM Standard D5388-93, 2013a, "Standard Test Method for Indirect Measurements of Discharge by Step-Backwater Method," ASTM International, West Conshohocken, PA, 2014, DOI: 10.1520/D5413-93R13, www.astm.org.

ASTM Standard D5413-93, 2013b, "Standard Test Methods for Measurement of Water Levels in Open-Water Bodies," ASTM International, West Conshohocken, PA, 2013, DOI: 10.1520/D5388-93R13, www.astm.org.

ASTM Standard D5541-94, 2014a, "Developing a Stage-Discharge Relation for Open Channel Flow," ASTM International, West Conshohocken, PA, 2014, DOI: 10.1520/D5541-94R14, www.astm.org.

ASTM Standard D3858-95, 2014b, "Standard Test Method for Open-Channel Flow Measurement of Water by Velocity-Area Method," ASTM International, West Conshohocken, PA, 2014, DOI: 10.1520/D3858-95R14, www.astm.org.

ASTM Standard D5130-95, 2014c, "Standard Test Method for Open-Channel Flow Measurement of Water Indirectly by Slope-Area Method," ASTM International, West Conshohocken, PA, 2014, DOI: 10.1520/D5130-95R14, www.astm.org.

Foth, 2021a, *Foth Standard Operating Procedure #2101*, Site Selection Criteria & Measurement with Velocity-Area Method.

Foth, 2021b, *Foth Standard Operating Procedure #2105*, Slope-Area Method.

Foth, 2021c, *Foth Standard Operating Procedure #2107*, Staff Gauge Installation and Water Level Monitoring.

Turnipseed, D.P., and Sauer, V.B., 2010. "Discharge Measurements at Gaging Stations," Techniques and Methods Chapter 8 of Book 3, Section A (3-8A), U.S. Geological Survey, Reston, VA. (Also available at http://pubs.usgs.gov/tm/tm3-a8/.)

United States Geological Survey, 1984, "Discharge Ratings at Gaging Stations", Chapter A10 Book 3 Applications of Hydraulics, U.S. Geological Survey, Reston, VA. (Also available at Discharge ratings at gaging stations (usgs.gov)).

United States Geological Survey, 2002. "Standards for the Analysis and Processing of Surface-Water Data and Information Using Electronic Methods". Water Resources Investigation Report 01-4044, U.S. Geological Survey, Reston, VA. (Also available at https://pubs.er.usgs.gov/publication/wri20014044)

Personnel Qualifications

A minimum of one qualified person is required to complete field measurements. A qualified person shall be someone who is formally trained in hydrology via an Accreditation Board for Engineering and Technology (ABET)-accredited engineering college or university and experienced in making open channel flow measurements. A qualified person may also be a technician lacking formal college training in hydrology but whom has been formally trained in open channel flow measurements using the procedures described in this SOP.

Personnel performing open-channel flow measurements shall have access to the project Health and Safety Plan (HASP). Note that the HASP may require a minimum of two people to be present when near water features such as rivers and streams.

Additional Health and Safety Training Recommendations:

- Field personnel shall have current CPR (Cardiopulmonary Resuscitation) and First Aid training.
- Field personnel shall have satisfied Occupational Safety and Health Administration (OSHA) training requirements (40 CFR 1910.120) if hazardous materials are known to be or may be present at the site.
- Field personnel shall have satisfied Mine Safety and Health Administration (MSHA) safety training requirements prior to making open channel flow measurements on a project site regulated by MSHA.

Equipment and Supplies

Required equipment will vary according to the measurement method and may include the following:

- Log-log graph paper (if using manual method)
- Microsoft Excel or other graphing software and computer (if using computer method)

Procedures

Background Information and Channel Conditions

Stage-discharge ratings most commonly involve relating discharge to stage at one location and use discharge measurements as the primary data for analysis (USGS, 1984).

Stage and Discharge Readings

Stream stage readings will be recorded per ASTM D5413-93 (ASTM, 2013b) and Foth SOP #2107 (Staff Gauge Installation and Water Level Monitoring). Stream flow rates adjacent to the staff gauges will be recorded and calculated by one of the following methods:

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- Velocity-Area Method, per ASTM Standard D3858-95 (ASTM, 2014b) and Foth SOP #2101 (Site Selection Criteria & Measurement with Velocity-Area Method).
- Slope-Area Method, per ASTM D5130-95 (ASTM, 2014c) and Foth SOP #2105 (Slope-Area Method)
- Other methods as approved.

Channel Hydraulics

The following channel hydraulic conditions should be taken into account when evaluating the development of a stage-discharge rating curve.

1. The stage-discharge relation at a gaging station is governed by channel conditions downstream from that point (referred to as 'control'). Knowledge of the channel features that control the stage-discharge relation is important in developing an accurate relationship curve, as the control feature(s) may change throughout the study period.
    a. Section Controls – A section control is a specific cross-section of the stream channel that controls the stage-discharge relation at that point in the channel. It can be a natural feature such as a rock ledge, sand bar, or severe channel constriction, or a man-made feature such as a small dam, weir, flume, or overflow spillway. Section controls can frequently be identified in the field by observing a riffle, or pronounced drop in the water surface as flow passes over the feature. If the feature becomes submerged due to higher flows, the riffle will no longer be visible, and it will cease to act as a control feature.
    b. Channel Controls – A channel control consists of a combination of features throughout a reach downstream from a gage, including channel size, shape, curvature, slope, and roughness. The length of channel reach that controls a stage-discharge relation varies; for steep channels it may be controlled by a relatively short reach, and for flat channels it may be controlled by a longer reach. The reach length will also vary depending on the magnitude of flow.
    c. Combination Controls – The stage-discharge relation may be governed by a combination of section and channel controls. This usually occurs for a short range in stage between the section and channel-controlled segments of the rating (known as the transition zone), and represent changes in slope or shape of a stage-discharge relation. Both section and channel controls can also occur at the same stage. In other instances, a combination control may consist of two section controls, where each has a partial controlling effect. Low flows are usually controlled by a section control, high flows are usually controlled by a channel control, and medium flows may be controlled by either.

Interferences

The following interferences may affect development of a stage-discharge rating curve.

1. The stage-discharge relation may be affected by the deposition or removal of stream bed or bank material by flowing water, usually at high flow conditions or manmade changes. Large changes may require a redefinition of the rating curve (example: creation/removal of a beaver dam). Small, transitory changes may be facilitated by adjustments to the stage observations (example: debris deposited on dam or bridge piling).

2. Aquatic growth may develop in a stream during the growing season, resulting in a temporary backwater situation. Adjustments to stage observations would normally be made during these periods.

3. Ice cover changes river hydraulics and alters the stage-discharge relation.

4. Hysteresis may affect the high flow stage-discharge relation when the water surface slope changes due to either rapidly rising or falling water levels. Hysteresis (sometimes referred to as 'loop ratings') is

most pronounced in relatively flat-sloped streams. The water surface slope on rising stages is significantly steeper than that for steady flow conditions, resulting in greater discharge than indicated by the steady flow rating. The reverse is true for falling stages. If discharge measurements are made at both rising and falling stages, a single curve splitting these measurements will generally result in satisfactory accuracy. It may be necessary to use separate curves for rising and falling conditions in extreme cases.

Stage-Discharge Rating Curve Development Procedures

The stage-discharge rating curve for the gage/cross-section of interest may be developed manually or by use of a computer program.

Manual Method

1. If sufficient current meter discharge measurements are available for the entire range in stage and discharge anticipated, the rating curve should be developed by plotting stage versus discharge on logarithmic plotting paper. Select a convenient stage scale so that all of the discharge measurements below bankfull stage plot in a relatively straight line. The graph can then be used to estimate future flow rates based on measured staff gage readings. Gauge height should be plotted on the Y-axis (USGS, 1984).

   For small streams with low flow that approach or reach zero, plot the low-flow component of the rating curve on rectangular coordinate plotting paper. See Section 10.1 and Figure 1 of ASTM D5541-94 (ASTM, 2014a) for additional details on typical rating curve shape and related flow components. Alternatively, the rating curve could be plotted on logarithmic paper, and an offset could be applied to account for zero or negative results (USGS, 2002).

2. If sufficient discharge measurements are not available for the entire range in stage and discharge that are necessary, develop a theoretical rating curve using the step-backwater test method in ASTM D5388-93 (ASTM, 2013a). This theoretical curve is plotted on logarithmic plotting paper along with the current meter measurements, and is used as a guide to shape the rating curve. Adjust the theoretical curve to go through the current-meter measurements, making separate adjustments to the upper, middle, and lower sections of the curve as necessary. Consideration should be given to how accurate the measurements are believed to be when adjusting the theoretical curve to fit those measurements.

Computer Method

Calculations can also be performed with the use of a spreadsheet associated with this SOP (SOP_#2106_Stream Flow_Stage-Discharge Relationship (2021).xlsx). The spreadsheet contains a sheet entitled “Regression” for entering stage and flow data. The data are then automatically graphed and a best-fit line and equation are automatically generated. The equation can then be used to estimate future flow rates based on measured staff gage readings. This is done by taking the best-fit equations from the “Regression” sheet, and entering them into the columns as noted on the “Stage-Flow Table” sheet. Note that the best-fit line should be reviewed and compared to the plotted data points to ensure that it is hydraulically accurate, as described in Sections 7.7 and 7.8 of USGS, 2002.

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Standard Operating Procedure

Staff Gauge Installation and Water Level Monitoring

Introduction

The purpose of this Standard Operating Procedures (SOP) is to establish standard field procedures for the installation of staff gauges and for recording surface water levels. These procedures apply to obtaining water levels in streams, lakes, wetlands, reservoirs, or other water bodies.

Stream stage is a critical parameter in the computation of stream discharge. Procedures for relating stage to discharge are found in Foth SOP #2106 (Stage-Discharge Relationship) (Foth, 2021b). Gauge heights are used as the independent variable in the stage-discharge relationship to compute discharge. Reliability of the discharge record is therefore dependent on the reliability of the gauge-height record.

A record of stream stage is also useful for designing bridges, embankments, or other structures, and in planning for the use of flood plains. Stage records of lakes and reservoirs also provide an index of feature surface area and volume.

This SOP describes equipment and methodology for the installation of staff gauges, and for the observation, sensing, and recording of stage in surface water features. This SOP focuses on the use of staff gauges and pressure transducers for stage measurements. Other methods are also available, as described in ASTM D5413-93 and in Sauer and Turnipseed, 2010. Among these are a gas-purge system (bubble gauge), as described in Sauer and Turnipseed, 2010.

References

ASTM Standard D5413-93, 2013. "Standard Test Methods for Measurement of Water Levels in Open-Water Bodies," ASTM International, West Conshohocken, PA, 2014, DOI: 10.1520/D5413-93R13, www.astm.org.

Foth, 2021a. *Foth Standard Operating Procedure #2101*, Site Selection Criteria & Measurement with Velocity-Area Method.

Foth, 2021b. *Foth Standard Operating Procedure #2106*, Stage-Discharge Relationship.

MNBWSR, 2013. "Hydrologic Monitoring of Wetlands", Hydrologic Monitoring of Wetlands, Minnesota Board of Water and Soil Resources Supplemental Guidance, March 2013.

Sauer, V.B., and Turnipseed, D.P., 2010. "Stage Measurement at Gaging Stations," Techniques and Methods Book 3, Chapter 7, Section A, U.S. Geological Survey, Reston, VA. (Also available at http://pubs.usgs.gov/tm/tm3-a7/.)

United States Army Corps of Engineers, 2012. "Staff Gage Setup Instructions", Omaha District Emergency Management, September 10, 2012. (Available at https://www.nwo.usace.army.mil/Media/Fact-Sheets/Fact-Sheet-Article-View/Article/487672/staff-gage-setup-instructions/).

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Washington State Department of Ecology, 2008. "Standard Operating Procedure EAP042, Version 1.2 – Measuring Gage Height of Streams", Washington State Department of Ecology, December, 2018. (Available at https://fortress.wa.gov/ecy/publications/SummaryPages/1803232.html).

Personnel Qualifications

A minimum of one qualified person is required to complete field measurements. A qualified person shall be someone who is formally trained in hydrology via an Accreditation Board for Engineering and Technology (ABET)-accredited engineering college or university and experienced in making open channel flow measurements. A qualified person may also be a technician lacking formal college training in hydrology but whom has been formally trained in open channel flow measurements using the procedures described in this SOP.

Personnel performing staff gauge measurements and installations shall have access to the project Health and Safety Plan (HASP). Note that the HASP may require a minimum of two people to be present when near water features such as rivers and streams.

Additional Health and Safety Training Recommendations:

- Field personnel shall have current CPR (Cardiopulmonary Resuscitation) and First Aid training.
- Field personnel shall have satisfied Occupational Safety and Health Administration (OSHA) training requirements (40 CFR 1910.120) if hazardous materials are known to be or may be present at the site.
- Field personnel shall have satisfied Mine Safety and Health Administration (MSHA) safety training requirements prior to making open channel flow measurements on a project site regulated by MSHA.

Equipment and Supplies

Staff Gauge Installation

- Style C Staff Gauge with 0.01-ft graduations and scaled 0.0 - 3.0 ft (or higher based on depth)
- ≥6' steel U-channel fence post (2.0 lb/ft)
- Hex. bolt or U-bolt (3½" x 5/16") (minimum 2 per staff gauge)
- Hex. nuts (5/16")
- Lock washer (5/16")
- Flat washer
- Fence post driver (optional if sledge hammer is used)
- Sledge hammer (minimum 8 lb) (optional if fence post driver is used)
- Bubble level (optional)
- Laser level instrument, tripod and stadia rod (or equivalent survey equipment/technique) (only used if tying staff gauge into site datum [recommended])
- Pressure transducer (optional)
- Zip-ties (optional; only used if installing pressure transducer)
- 5' of fishing line (≥10-lb test), cord, or metal wire (16-gauge or larger diameter) (optional; only used if installing pressure transducer)
- Waterproof boots
- USGS-approved personal flotation device
- Sharpie or waterproof marker
- Field Log Book

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Water Level Recording

- Waterproof boots
- USGS-approved personal flotation device
- Survey rod or portable staff gauge (optional; used only if staff gauge is compromised)
- 5-gallon bucket, hacksaw, and cordless drill (optional; use to create a makeshift stilling well)
- Laptop computer and transducer docking device (if pressure transducer is being used)
- Sharpie or waterproof marker
- Field Log Book

Procedures

Staff Gauge Installation

Staff Gauge Site Selection

The staff gauge site installation location should be based on the following criteria:

- Site selection criteria contained in Foth SOP #2101 (Site Selection Criteria & Measurement with Velocity-Area Method) (Foth, 2021a) for stream flow measurements should be followed.
- Select a location that is readily and safely accessible for ease of installation and safety during recording of the surface water elevation.
- Select a location free of debris and rock or other structure interference.
- Select a location where flow velocity is low and not subject to significant turbulence. However, the velocity should not be so low such that sediments will collect around the staff gauge base. Alternatively, a stilling well could be installed surrounding the staff gauge, as described in subsequent sections of this SOP.
- Install the gauge where it will be visible during all stage conditions, and will capture the ranges of stages expected.
- Install the gauge with the flat face in the direction of stream flow if possible, to prevent water from building up on the gauge face.
- The staff gauge (and stilling well, if used) can be attached to a bridge or other structure, provided the other site selection criteria are met as closely as possible. If located at or near a bridge, it should be on the downstream side. If this is not possible and it must be located on the upstream side, it should be placed far enough upstream to be out of the zone of drawdown caused by the bridge during medium and high water levels.
- If the gauge is installed for the purpose of measuring stage in a lake or reservoir and it is located near an outlet structure, locate the gauge upstream of the zone of drawdown of the outlet structure.
- If tying the staff gauge elevation into the site datum (recommended), ensure that site conditions are such that an accurate datum can be maintained. Appropriate reference marks should be located both on and off the gauging structure to maintain accurate level surveys of the gauge.

Staff Gauge Style Selection

Examples of common staff gauge styles available are shown below in Diagram 1. Foth most typically installs Style C, with 0.01-foot graduations (black tick marks every 0.02 feet) and three feet of scale (measurable water depth).

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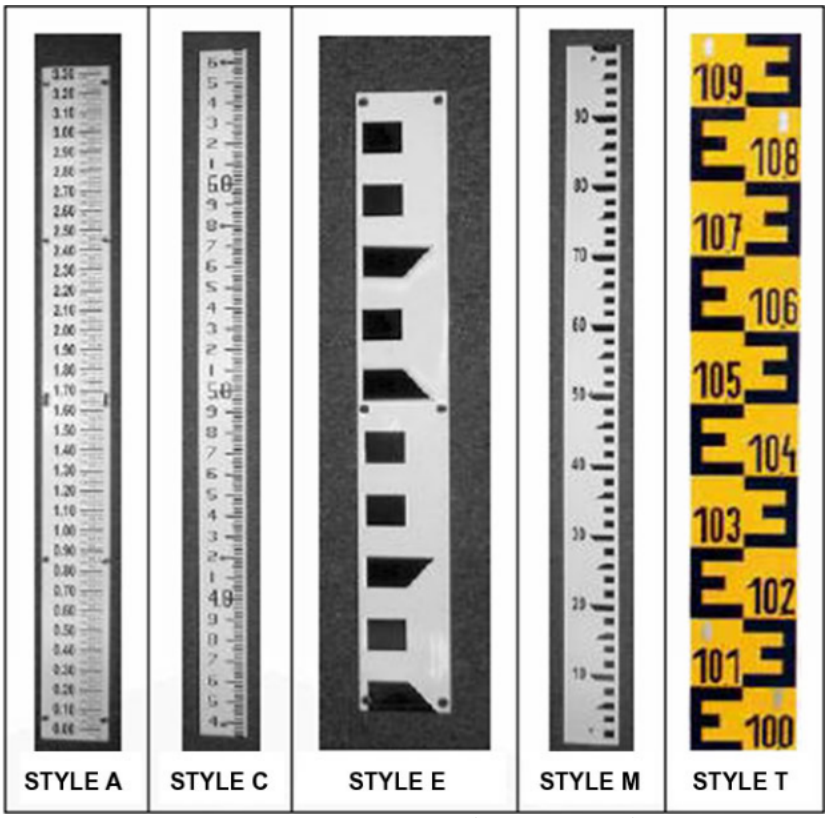


Diagram 1. Typical Staff Gauge Styles (USACE, 2012)

Pressure Transducer Selection

The installation of a pressure transducer on a staff gauge is optional but recommended. A pressure transducer with corresponding datalogger will allow water depth to be recorded at a more frequent interval than with manual measurements, allowing a more accurate stage-storage curve to be developed with a higher level of confidence.

A number of submersible pressure transducers are commercially available for use in groundwater monitoring wells. However, a transducer installed on a staff gauge will be subject to different environmental conditions than in a monitoring well. It should be verified with the manufacturer that the transducer selected for a staff gauge installation can properly function within the range of temperatures and ponding levels anticipated at the gauge location, particularly considering that the transducer may experience dry conditions during times of zero flow/ponding. If installed in northern climates, the transducer should be removed prior to winter freeze-up as most units will be damaged or destroyed in freezing conditions.

Foth owns select pressure transducers and rents others from a number of firms. In addition to the ability to withstand the environmental conditions described above, transducer selection should consider ease of deployment, data retrieval, and data download. In particular, technology that allows for remote data download (without having to remove the transducer and place onto a docking station connected to a computer) will simplify data download and reduce errors associated with transducer reinstallation at a consistent elevation. For additional information on transducer selection, as well as alternatives to pressure transducers (e.g. acoustic sensors, radar, laser, etc.), see ASTM, 2013 and Sauer and Turnipseed, 2010.

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Staff Gauge Installation Procedures

The following steps should be taken for staff gauge installations (additional detail is available in MNBWSR, 2013):

1. If using fence post driver to install fence post, attach only the bottom of the staff gauge to the fence post using hex. bolts, nuts, and washers. If using sledge hammer, both the bottom and top of the staff gauge can be secured to the fence post.

2. Regardless of device used to drive fence post, install staff gauge such that a minimum of 1.0 feet of the fence post can be driven into the sediment, and so that the 0.0-ft staff gauge mark matches the top of sediment (see Figure 1 in Attachment 1).

3. Install the staff gauge as vertical as possible. Use a bubble level to confirm the staff gauge is vertically true.

4. Once fence post is securely installed in the sediment secure the top of staff gauge to fence post with hex. bolts, nuts, and washers (see Figure 1 in Attachment 1).

5. If the staff gauge is to be tied into the site datum (recommended), use level and rod to tie into site benchmark using standard survey techniques. At the staff gauge location, hold the survey rod against the gauge with the bottom at the water surface and take a reading. Then record the water level on the staff gauge. The benchmark elevation can then be transferred to this reference point on the staff gauge, and the water depth can then be subtracted from that elevation to obtain the elevation at the 0.0-ft mark on the staff gauge. Note that if the 0.0-ft mark does not align with the top of sediment, the off-set will need to be taken into account when determining stream bed elevation.

6. If installing a pressure transducer, program the unit prior to deployment. When installing the unit, the sensor portion of the transducer should be placed at the 0.0 ft mark of the staff gauge (such that the transducer readout in feet of head will correspond to the same value with manual staff gauge reading). Affix the pressure transducer to the staff gauge with plastic zip-ties or with another similarly secure method. Ensure that the transducer is securely fastened such that the transducer maintains a consistent elevation during the entire deployment. Also consider zip-tie/fastener placement such that the transducer can be returned to the exact elevation following data download.

7. If waves or turbulence make reading the staff gauge difficult, a stilling well could be installed around the staff gauge and/or transducer. A stilling well is a pipe or chamber connected by small openings to the main water surface being measured. It serves to dampen transient fluctuations in water levels due to waves or turbulence and simplify water level measurements. See the 'Water Level Recording' section of this SOP for instructions on installing a makeshift stilling well using a five-gallon bucket.

Water Level Recording

The following procedures should be used to record water levels from a staff gauge (see Diagram 2 for example):

1. Note the foot label above the water line and subtract 1 foot.

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2. Note the tenth label above the surface water line and subtract 1 tenth.

3. Count the hundredth hashes down to the water surface. Subtract the number from 10 and record that number.

4. Record the surface water value in the field log book.

5. If a pressure transducer is installed, remove the unit from the gauge (unless remote sensing technology is being used) and download the data according to manufacturer specifications. When returning the unit to the staff gauge, it is essential that the transducer sensor be installed at the exact elevation as previously installed (i.e. sensor at gauge 0.0 ft mark), and that the sensor be securely fastened to the gauge. Zip-ties and a magic marker can help with this effort.

Additional notes on recording water levels:

- At every water level measuring event, make a visual inspection of the staff gauge and surrounding conditions, and note in the field log book any apparent damage or conditions that could affect water level measurement, such as debris or sediment build-up.

- If water levels fluctuate on the staff gauge scale, note the average reading in the field log book, along with the range of water level fluctuation. In situations where the fluctuation is excessive and no permanent stilling well has been installed, employ a makeshift stilling well. A makeshift stilling well can be created with a five-gallon bucket with the bottom cut out and a cut up the side, to permit spreading of the bucket walls to surround the staff gauge structure. Open the bucket walls and wrap the bucket around the staff gauge with the bottom of the bucket walls at a depth of 0.5 to 1.0 feet.

- For alternate methods for measuring water level (e.g. laser level, tape-down from bridge, etc), see Washington Dept. of Ecology, 2018.

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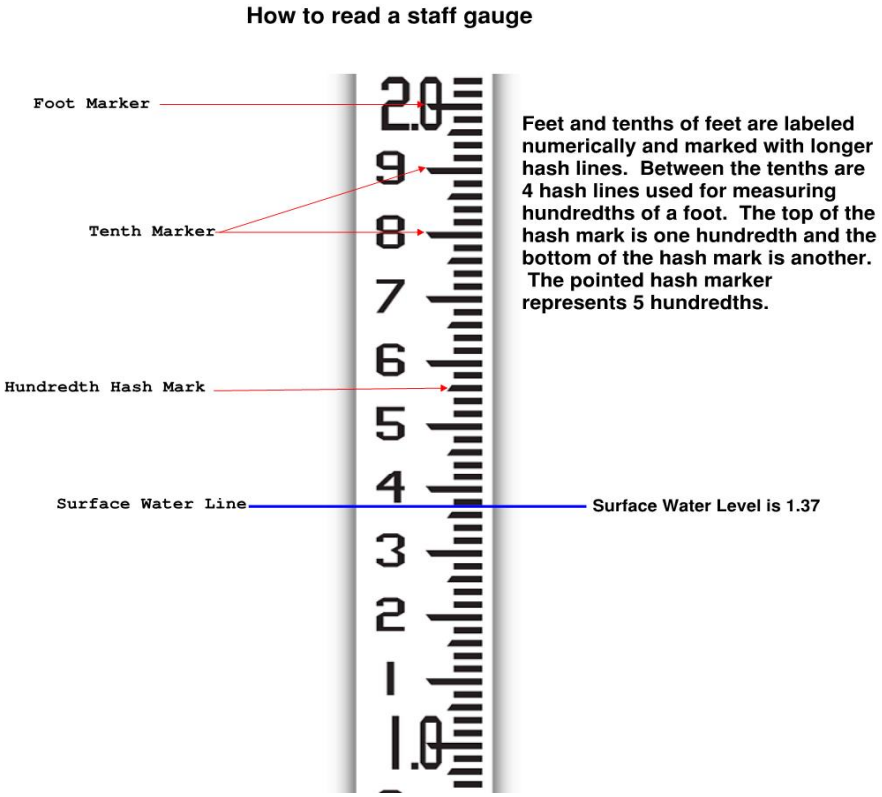
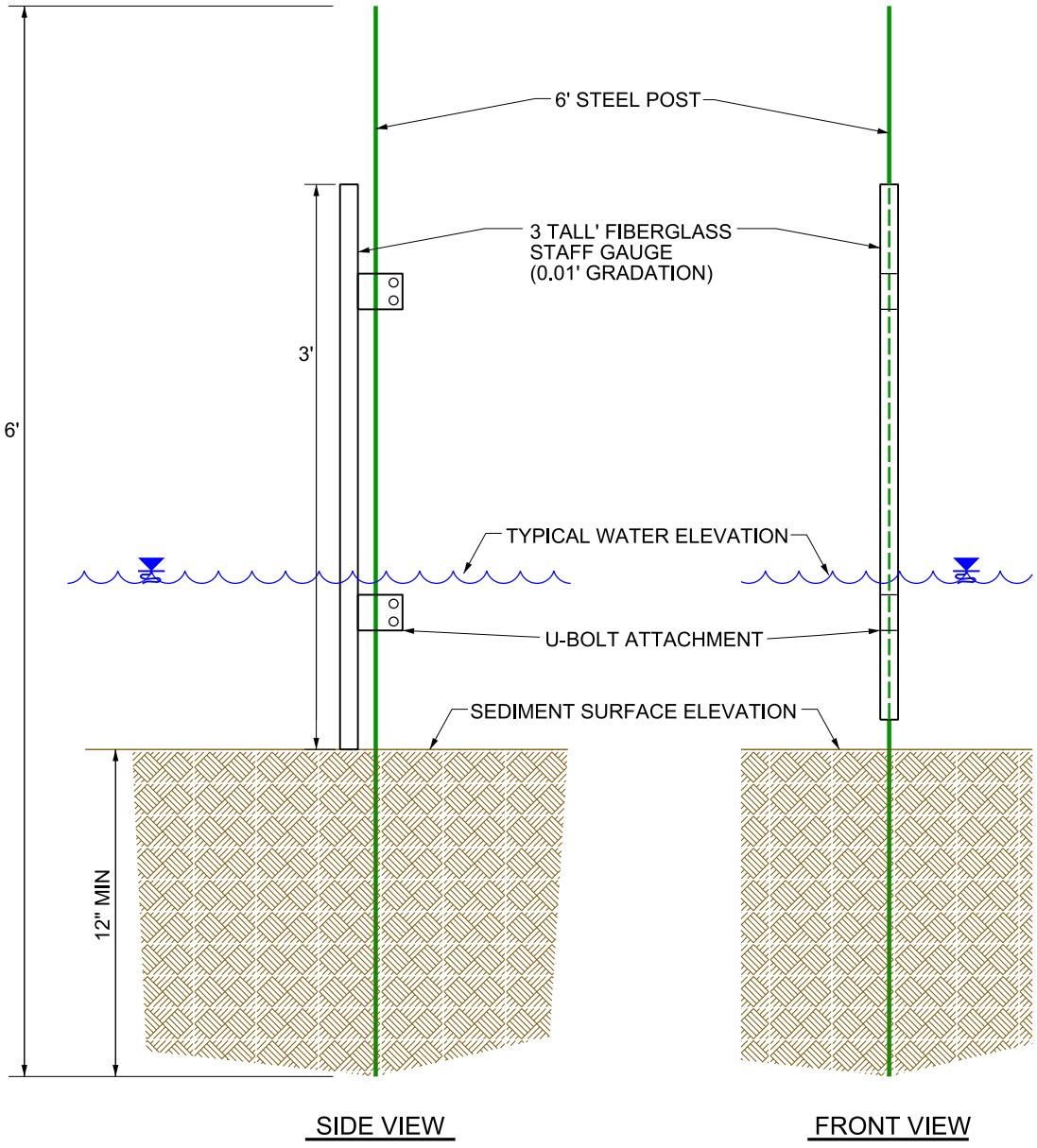


Diagram 2. Staff Gauge Water Level Reading Example

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Attachment 1

Staff Gauge Installation Detail Figure



STAFF GAUGE INSTALLATION SOP

FIGURE 1

TYPICAL STAFF GAUGE INSTALLATION DETAIL

Foth

NOT TO SCALE

Date: MAY 2020	Revision Date:	
Drawn By: TRN	Checked By: MAN	Project: SOP

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Standard Operating Procedure

AquaTROLL® 600 Multiparameter Sonde

Introduction

The purpose of this Standard Operating Procedure (SOP) is to establish a standard procedure for operating the Aqua TROLL® 600 Multiparameter Sonde (Aqua TROLL® 600) by In-Situ® Inc.

For many environmental applications, the Aqua TROLL® 600 meets all of the required operating parameters:

- Multi-parameter sensor, telemetry, cloud-based data management software to monitor: Temperature, pH, ORP, Conductivity, Dissolved oxygen,
- Fits in 2-inch wells.
- Minimal sensor maintenance/drift to extend deployments.
- Power supply must last longer than three months between site visits.
- Visual data management system filters data by parameter, site, and date range to enable remote decision-making.

The Aqua TROLL® 600 is the latest model of water quality instruments that includes Aqua TROLL® and other TROLL products by In-Situ®. These sondes are used to measure multiple field parameters in flowing or still water conditions. Suitable sample settings include streams, rivers, lakes, ponds, groundwater wells, and other water sources. This instrument can be deployed on either a short term or long term application.

This instrument is set-up to measure pH, specific conductance, oxidation reduction potential (ORP), dissolved oxygen, temperature, and depth (pressure). Specifications for each parameter are provided in Attachment 1.

Additional equipment necessary to operate the Aqua TROLL® 600 includes Android cell phone with VuSitu™ Mobile App or laptop computer with Win-Situ 5 for digital reading of the data during instrument deployment along with a TROLL Com device (Bluetooth or hardwire). Also provided is a weighted sensor "restrictor" or a flow through cell to protect the sensors during active data acquisition, a RuggedCable between the Aqua TROLL® 600 and the Tube 300R Telemetry System, and the Tube 300R unit.

Use of the Tube 300R Telemetry System and HydroVu Internet is an option to integrate AquaTROLL 600 data collection with real-time remote data download, viewing, and evaluation. Use of this option may have advantages for projects, but is not essential. The advantages and disadvantages for use of remote telemetry should be considered before procuring and deploying this equipment. Some advantages and disadvantages for use of remote telemetry with the AquaTROLL 600 are included within the procedures discussed below. For the operation of the Tube 300R Telemetry System, refer to the owner's manual. Although Bluetooth/wireless remote connection is an option, separate cables are also provided for hardwire connection of the Tube 300R or the Aqua TROLL® 600 directly (and independently) to a laptop computer.

Remote connection of Aqua TROLL® instrumentation is a flexible means of obtaining data when the instrument is at a distant and/or below-ground location. Bluetooth connection of the Aqua TROLL® 600 is established via an internal communication system. If the Aqua TROLL® 600 is deployed below ground, a surface connection can be established using a Wireless TROLL Com device by Bluetooth or hardwire.

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Wireless data collection from the Tube 300R is accomplished via HydroVu Internet, Web-based software. This software is accessible on any device that can access the Internet and affords data visualization or download.

The Aqua TROLL® 600 instrument has the capability of expanding the parameters list by purchasing additional sensors for measurement of turbidity, ammonium, chloride, and nitrate. Additional water quality parameters are added by removing existing sensors.

Proper operation of all Aqua TROLL® 600 instrumentation is based on the meter specific manuals (Attachment 1), and includes care and maintenance, calibration, and proper handling during the measurement.

References

Aqua TROLL® 600 Multiparameter Sonde Quick Start Guide, March 2017, Revision 3.

Tube 300R Telemetry System Quick Start Guide, July 2016, Revision 7.

Aqua TROLL® 600 Multiparameter Sonde Operator's Manual, August 2016, Revision 3.

Tube 300R Telemetry System Owner's Manual.

Personnel Qualifications

The personnel qualifications should be directed in the project planning document (PPD) and Health and Safety Plan (HASP) and appointed by the project manager (PM). A minimum of one person is required to complete sampling and should be trained in this SOP technique. They should understand methods for reporting or recording data.

Additional Health and Safety Training Requirements for field personnel:

- Current Cardiopulmonary Resuscitation (CPR) and First Aid training.
- Satisfied Occupational safety and Health Administration (OSHA) training requirements (40 Code of Federal Regulations [CFR] 1910.120) if hazardous materials are expected.
- Satisfied Mine Safety and Health Administration (MSHA) requirements if working on a project site regulated by MSHA.

In-Situ® Inc. Technical Support: 970-498-1566

General contact information:
In-Situ® Inc., 221 East Lincoln Ave., Fort Collins, CO 80524; 800-446-7488; www.In-Situ.com.

Equipment and Supplies

- Aqua TROLL® 600 Multiparameter Sonde.
- RuggedCable.
- Wireless TROLL Com.
- Tube 300R Telemetry System and cable.
- Deionized water.
- Battery charger or spare batteries (see Attachment 1).
- Calibration solution (see Attachment 1).

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Procedures

General Procedures

The general maintenance, deployment considerations, and troubleshooting procedures are provided in several sections of the owner's operation manual, and the main sections are provided in Attachment 1.

Proper operation requires keeping the sensors from drying out, ensuring the rechargeable batteries are fully charged, and proper sensors are calibrating. **For calibration of each sensor, refer to the user owner's manual (Attachment 1).**

No measurements in water are acceptable unless the meter is properly calibrated and the meter is providing a stable reading. Improper calibration may result in erroneous readings. The operator should know common ranges for the measured parameters. Since the measurements are temperature compensated, erroneous values of temperature will likely mean that other readings are in error too. Air bubbles, excessive solids, oil and grease, and other substances can interfere with the readings. A note should be provided if the sampled water is found to contain potential interfering substances. Spare batteries should be on hand since measurements with the low battery indicator may be faulty.

The sensors should be thoroughly rinsed between readings. For cleaning and care of the unit, refer to the manual. Deionized water and other solutions should be on hand.

In cases of high flow, the stream force or pull on the instrument may be extreme – and there is a risk of losing the probe or damaging the cable connection. The manual includes methods for monitoring in high flow situations.

The use of the instrument for water profiling with depth requires some calibration of the depth measurement (provided by a pressure transducer). Care should be taken to lower the unit at a rate that allows a stable reading at each depth.

Unique Setup and Connection Procedures

Because the Aqua TROLL® 600/Tube 300R instrumentation includes several integrated components and several communication options, the most common setup and connection procedures are listed below in summary form for clarification since the manuals in Attachment 1 hide the simple procedures in the details. For new users, it is recommended that you call In-Situ, Inc. Tech Support to guide you through the setup process: 970-498-1566. **[*Have a photo (.bmp) of the site location and survey elevation of each point ready at setup.*]**

1. HydroVu Setup (Best set in office environment). Use Google Chrome and start **www.HydroVu.com**.
    a. Username: Heather.hallett@foth.com
    b. Password: **Foth123**
2. Add Locations in "Location" menu tab, mapped setup with latitude/longitude entry. [This will be needed later during Aqua TROLL® 600 setup.]
    a. Pair Aggregator Serial (Tube 300R) and Instrument Serial (Aqua TROLL® 600). This will need to be done for each sensor depending on setup.
        i. If this step is not done properly, the data will still send to HydroVu but under default *serial number*.
    b. Define projects and labels while still in "Location" menu tab.

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c. Remove old locations paired to newly assigned aggregator/instrument.

d. Refresh screen view with F5 to view changes.

3. **Aqua TROLL® Setup** (Can be set in office or field environment).

   a. Install batteries in the Aqua TROLL® 600 (2 D-size, new).

   b. Connect Aqua TROLL® 600 to computer via wireless TROLL Com.

   c. Start Win-Situ 5 Software.

      i. Set up Modbus according to "Quick Start Guide."

      ii. Calibrate Sensors as described in User's Manual. Note there is a difference in calibration between vented and non-vented equipment.

      iii. Set up a Data Site.

      iv. Set up a Data Log; make sure all needed sensors are activated.

      v. Data Log has multiple parts. Each probe will have its own data collection frequency that needs to be set as the same or shorter than the telemetry unit (Tube 300R). The telemetry unit data send/collection can be updated through HydroVu remotely, as needed.

   d. Connect RuggedCable from Aqua TROLL® 600 to Tube 300R Telemetry System.

4. **Tube 300R Setup** (Can be set in office or field environment).

   a. Connect Tube 300R to the computer.

   b. Follow setup directions in Attachment 1, "Quick Start Guide."

   c. Set site name and clock; save settings.

   d. Set probe reading schedule; save settings.

      i. Set data collection and upload frequency. Can be changed remotely via HydroVu, if needed.

   e. STOP and RESTART Tube 300R and Test Communications. (Follow communications tests as noted in Attachment 1, "Quick Start Guide."

5. Deploy the Aqua TROLL® 600 and Tube 300R.

   a. AquaTROLL/Tube 300R field tricks [Don't forget to read these BEFORE you mobilize or procure equipment.]

      i. Pre-check cell phone signal is of adequate strength for communications before attempting deployment. In some areas, cell phone coverage or cell p hone reception is inadequate for reliable communication. This is an indicator that the Tube 300R will also have difficulty communicating and uploading data to the HydroVu web site. If signal strength is poor only periodic communication may be possible or no data transfer during setup may be possible. In this case, you may need to rely on only AquaTROLL 600 data collection without telemetry. You may consider using an auxiliary antennae or signal booster if the existing signal is weak.

ii. Ensure there is a method to attach the AquaTROLL/Tube 300R cable to the top of the well cap or cover (i.e., a J-Plug with eye bolt/carabineer clip, or slip cap/eye bolt/carabineer clip).





b. Minimize support cable/rope diameter(s) for equipment suspended beneath the Tube 300R to ensure the cable/rope will fit between the Tube 300R device and the inside of the well casing.

c. Position the instrument.

d. Verify instrument depth.

e. Secure the cable at the well head.

6. Check HydroVu upload from Aqua TROLL®/Tube 300R is occurring.

   a. This can be done by setting upload frequency to shorter time to see uploads more frequently and then changing upload frequency via HydroVu to final upload frequency after upload has been verified.

Unique Disconnection, Demobilization, and Storage Procedures

Because the Aqua TROLL® 600/Tube 300R instrumentation includes several integrated components and several communication options, the most common demobilization and disconnection procedures are listed below in summary form.

1. **HydroVu Project Close Out** (Best closed in office environment).

   a. Use Google Chrome and start www.HydroVu.com.

   b. Check HydroVu upload from Aqua TROLL®/Tube 300R has occurred.

   c. Download all current site data that need to be saved. [This is a backup, as three other data downloads may also occur during demobilization.]

2. **Aqua TROLL® 600 and Tube 300R Removal from Well.**

   a. Remove well cover and cap and pull instruments from the well by the hanger, not the cables.

   b. Decontaminate equipment exterior while removing from well according to HASP.

   c. Once Aqua TROLL® 600 is removed from well, reverse the restrictor and end cap to fully enclose the sensors.

   d. Store equipment in container or heavy plastic bag(s) as the equipment is disconnected until more thorough inspection and cleaning can be done in the office.

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3. **Tube 300R Demobilization** (Can be performed in office or field environment)
    a. Connect Tube 300R to the computer (port is on top of Tube 300R, next to antennae).
    b. Download data, as needed.
    c. Stop the Tube 300R communications via ANT software in “functional mode and test” tab.
    d. Tube 300R communications can be restarted, but this is not necessary until the next project starts.
    e. Disconnect RuggedCable from Tube 300R and Aqua TROLL® 600; roll and store.
4. **Aqua TROLL® Demobilization** (Can be performed in Office or Field environment).
    a. Connect Aqua TROLL® 600 to Computer via Wireless TROLL Com and start Win-Situ 5 Software (connect Wireless TROLL Com directly to Aqua TROLL® 600).
        i. Ensure log has stopped; if not, manually stop the current log.
        ii. Download and export data from current log; and other logs, as needed.
    b. Close Win-Situ 5 and disconnect Aqua TROLL® 600 from Computer.
    c. Inside Battery Compartment:
        i. Remove batteries from the Aqua TROLL® 600 (2 D-size).
        ii. Replace desiccant packet if existing packet has turned pink.
        iii. Remove secure digital (SD) card located just above the positive side of batteries, and download data logs to computer for backup.
        iv. Replace SD Card.
    d. Store sensors. (Remove and reattach restrictor before and after this step.)
        i. Wash probes with clean water, and inspect probes; maintain if needed.
        ii. Do not remove pH/ORP probe, but retain some liquid in restrictor.
    e. Place Aqua TROLL® 600 in storage box labeled with Instrument Serial Number (ISN).

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Attachment 1

Aqua TROLL® 600 Mulitiparameter Sonde Owner's Manual

Aqua TROLL 600

Operator's Manual



Information subject to change without notice. In-Situ, In-Situ logo, Baro Merge, BaroTROLL, HERMIT, HydroVu™, iSitu, Pocket-Situ, RDO, RuggedCable, RuggedReader, SmarTROLL™, TROLL, VuSitu, and Win-Situ are trademarks or registered trademarks of In-Situ Inc.©2016. All rights reserved. This product may be covered by patents identified at www.in-situ.com/patents

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Introduction

Serial Number Location

The instrument serial number is on the product label affixed to the instrument body. Serial numbers for individual sensors are engraved on the sensor body.

Instrument Description

The Aqua TROLL 600 uses the latest sensor and electronics technology to provide laboratory-quality measurements for field use. Parameters include water level, pH, dissolved oxygen, and more. The instrument fits inside wells as small as 2" in diameter. The water level/pressure sensor and barometric pressure sensor are integrated into the sonde. Additional sensors may be selected and replaced to suit your project's needs. An optional motorized sensor wiper may also be included on the instrument.

Use the Aqua TROLL 600 for long-term monitoring in freshwater and marine environments. It's also ideal for the following applications:

- Groundwater sampling
- Low-flow testing
- Mine water monitoring
- Stormwater management

The built-in LCD screen displays battery status, connectivity info, and other vital information. Setup is easy with the VuSitu app and a Bluetooth-enabled mobile device. The Aqua TROLL 600 can record data to an internal micro SD card and works with telemetry devices for remote monitoring.

Document Conventions

Throughout this document you will see the following symbols:



A checkmark highlights a tip or feature.



The exclamation point calls your attention to a requirement, safety issue, or important action that should not be overlooked.

Unpacking and Inspecting

Your equipment was carefully inspected before shipping. Check the equipment for any physical damage sustained during shipment. Notify In-Situ and file a claim with the carrier if there is any such damage; do not attempt to deploy or operate the instrument.



Save packing materials for future storage and shipping of your equipment.

Accessories may be shipped separately and should be inspected for physical damage and order fulfillment.

Obtaining Repair Service

If you suspect your system is malfunctioning and repair is needed, you can help assure efficient servicing by following these guidelines:

1 Call or email In-Situ Technical Support. Have the product model and serial number available.

2 Be prepared to describe the problem, including how the product was used and the conditions noted at the time of the malfunction.

3 If Technical Support determines that service is needed, they will ask your company to fill out the RMA form and pre-approve a specified monetary amount for repair charges. When the form and pre-approval is received, Technical Support will assign an RMA (Return Material Authorization) number.

4 Clean the product as described in the manual.

5 If the product contains a removable battery, remove and retain it unless you are returning the system for a refund or Technical Support states otherwise.

6 Carefully pack your product in its original shipping box, if possible.

7 Mark the RMA number clearly on the outside of the box.

8 Send the package, shipping prepaid, to:

In-Situ:
ATTN: Repairs
221 East Lincoln Avenue
Fort Collins, CO 80524

The warranty does not cover damage during transit. In-Situ recommends insurance for all shipments. Warranty repairs will be shipped back prepaid.

Outside the U.S.

Contact your international In-Situ distributor for repair and service information.

Guidelines for Cleaning Returned Equipment

Please help us protect the health and safety of our employees by cleaning and decontaminating equipment that has been subjected to potential biological or health hazards, and labeling such equipment. Unfortunately, we cannot service your equipment without such notification. Please complete and sign the form (or a similar statement certifying that the equipment has been cleaned and decontaminated) and send it to us with each instrument.

1 We recommend cleaning with only mild soaps that are compatible with the product materials. Wetted materials lists are provided on the product specification sheets. Clean all cables and remove all foreign matter.

2 Clean the cable connectors with a clean, dry cloth. Do not submerge the connectors.

3 Clean the instrument including the nosecone, cable head, and protective caps.



If an instrument is returned to our Service Center for repair or recalibration without a statement that it has been cleaned and decontaminated, or if it is the opinion of our Service Representatives that the equipment presents a potential health or biological hazard, we reserve the right to withhold service until proper certification is obtained.

Decontamination & Cleaning Statement

Company Name		Phone
Address		
City	State	
Instrument Type		Serial Number
Contaminant(s) if known)		
Decontamination procedure(s) used		
Cleaning verified by		Title
Date		

Safety

Read the safety information on this page before deploying or configuring your Aqua TROLL 600. If you have questions, contact In-Situ Technical Support for assistance.

- Use D-cell alkaline batteries.
- Do not use the Aqua TROLL 600 in any manner not specified by the manufacturer.
- Do not use batteries of different ages or types.
- Do not submerge the Twist-Lock connector ends of the cable or instrument when they are not connected.
- Do not submerge the Wireless TROLL Com or your mobile device in liquid.
- Ensure that sensors or sensor plugs, are completely inserted into the ports, so that no liquid can enter the instrument.
- Ensure that the RDO Sensor Cap is pressed firmly over the sensor lens and is flush with the instrument before submerging in liquid.
- Replace the cable if insulation or connectors are damaged.
- Make sure the probe and sensor O-rings are clean and free of damage.

Intended Use

The Aqua TROLL 600 multiparameter sonde is designed to be safe:

- during indoor or outdoor use;
- when used at altitudes up to 2000m;
- in ambient temperatures from -5 to 50C;
- in any relative humidity levels;
- during transient voltages up to the levels of Overvoltage Category III.

If the equipment is used in a manner not specified by the manufacturer, the protection provided by the equipment may be impaired.

Instrument Specifications

Operating temperature	-5 to 50° C (23 to 122° F)
Storage temperature	Components without fluid: -40 to 65° C (-40 to 149° F) pH/ORP probes: -5 to 65° C
Dimensions	4.7 cm (1.85 in.) OD x 60.2 cm (23.7 in.) with restrictor installed (including connector) With bail: 73.9 cm (29.1 in.)
Weight	1.45 kg (3.2 lbs) - includes all sensors, batteries, bail
Wetted materials (sonde and sensors)	Ceramic, Delrin™, Inconel™, PC, PC alloy, Platinum, Nylon, Santoprene™,Titanium, Viton™
Environment rating	IP68 with all sensors and cable attached. IP67 with sensors removed, battery cover removed, or cable detached
Max pressure rating	Up to 350 PSI
Communication	RS485/MODBUS, SDI-12, Bluetooth®
Reading rate	1 reading every 2 seconds for one parameter, no wipe
Internal memory	16 MB
Additional memory, micro SD card[2]	16+ GB included, any size micro SD up to 32 GB accepted
Logging rate	1 minute to 99 hours
Logging modes	Linear, Linear Average, Event
Data logging	50 logs (defined, scheduled to run, or stored)
LCD screen	Integrated display shows status of sonde, sensor ports, data log, battery, and connectivity
Internal power Battery life[3]	(2) user-replaceable D-cell alkaline batteries > 6 months typical with wiping > 9 months typical without wiping
External power voltage[4] External power current[4]	8-36 VDC (required for normal operation) Sleep: < 0.2 mA typical Measurement: 40 mA typical, 75 mA Max
Interface	Win-Situ 5 Software, VuSitu Mobile App on select mobile devices using Android 4.4 with Bluetooth 2.0
Cable	Vented or non-vented polyurethane or vented Tefzel®
Hex screw driver	0.050 in. (1.3 mm)

Software interface	Android: VuSitu through Google Play Windows: Win-Situ 5 Data Services: HydroVu
Interface	Android 4.4, requires BlueTooth 2.0
Certifications	CE, FCC, WEEE, RoHS Compliant
Warranty	2 year - sonde, sensors (excluding pH/ORP); 1 year - pH/ORP sensor Other - see warranty policy at www.in-situ.com
Notes	Specifications are subject to change without notice. Android is a trademark of Google, Inc. Bluetooth is a trademark of Bluetooth SIG, Inc. Delrin and Tefzel are trademarks of E.I. du Pont de Nemours & Co. Santoprene is a trademark of ExxonMobile. Inconel is a trademark of Special Metals Corporation. Viton is a registered trademark of DuPont Performance Elastomers L.L.C.

[1]For 30 parameters>100,000 data records, > 3 years at 15 minute interval. A single data record includes timestamp, temperature, RDO, pH, ORP, turbidity, and conductivity logged in Linear or Linear Average mode.

[2]Log data recorded to SD card in comma delimited variable (CSV) file format.

[3]Logging all sensors at 15 minute interval on 2 D-cell alkaline batteries. Battery life dependent on site conditions and wiping.

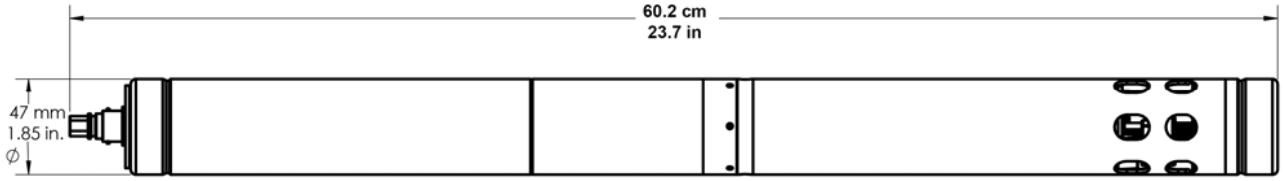
[4]Dependent on display and wiping

External Power Source Requirements



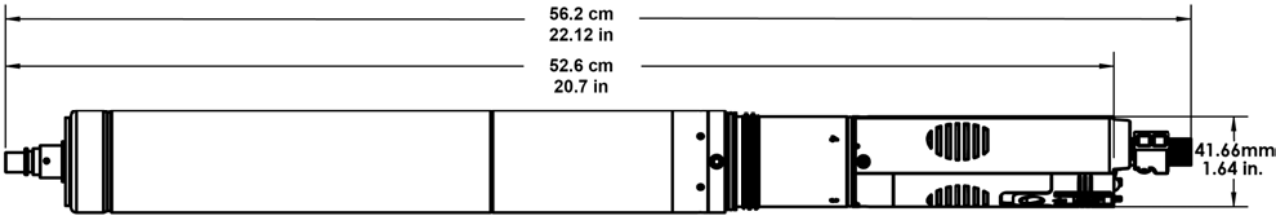
Current from an external power source must not exceed 4 amps.

Instrument Dimensions with Restrictor On



Total length with connector	60.2 cm (23.7 in)
Diameter	47 mm (1.85 in)

Instrument Dimensions with Restrictor Off



Total length with wiper brush on	60.2 cm (23.7 in)
Total length with wiper brush off	47 mm (1.85 in)
Diameter	41.66 mm (1.64 in)

Sensor Specifications

Sensor Summary

Sensors	Expected Lifetime*	Recommended Calibration Frequency	Pressure Rating - PSI	Usable Depth		Operational Temperature Range
pH/ORP	2 years or greater**	10 to 12 weeks**	350	200	650	- 5 to 50° C
RDO	2 years or greater	12 months**	350	200	650	- 5 to 50° C
Conductivity	2 years or greater	User calibration only if needed	350	200	650	- 5 to 50° C
Temperature	2 years or greater	NA	350	200	650	- 5 to 50° C
Turbidity	2 years or greater	User calibration only if needed	350	200	650	- 5 to 50° C
Pressure	2 years or greater	User calibration only if needed	12.8 42.7 108 285	9 30 76 200	30 100 250 650	- 5 to 50° C
Barometric Pressure	2 years or greater	User calibration only if needed	NA	NA	NA	- 5 to 50° C
Ammonium	6 to 12 months**	Monthly**	30	25	70	0 to 40° C
Chloride	1 year or greater**	Monthly**	350	200	650	0 to 50° C
Nitrate	6 to 12 months**	Monthly**	30	25	70	0 to 40° C
Chlorophyll a	2 years or greater	User calibration only if needed	350	200	650	- 5 to 50° C
BGA-PC	2 years or greater	User calibration only if needed	350	200	650	- 5 to 50° C
BGA-PE	2 years or greater	User calibration only if needed	350	200	650	- 5 to 50° C
Rhodamine	2 years or greater	User calibration only if needed	350	200	650	- 5 to 50° C
Fluorescein	2 years or greater	User calibration only if needed	350	200	650	- 5 to 50° C
FDOM	2 years or greater	User calibration only if needed	350	200	650	- 5 to 50° C
Crude Oil	2 years or greater	User calibration only if needed	350	200	650	- 5 to 50° C

* Expected lifetime includes total shelf life and deployment lifetime.

** Lifetime and calibration frequency depend on site and storage conditions.

Solutions

Solution	Shelf Life - Unopened	Shelf Life - Opened
Quick Cal	4 months. Store in a cool, dark place. Shake before use.	7 to 21 days (±10 mV, ±0.05 pH, ±50 µS/cm)
ZoBell's	9 months. Store in a cool, dark place.	3 to 6 months
Low Conductivity (147 µS/cm)	12 months	Hours (±1 µS/cm, check before use)
Other Conductivity	12 months	3 to 6 months
pH Calibration Buffers	24 months	3 to 6 months
Sensor Reference Filling Solution	24 months	12 months
pH Storage Solution	24 months	12 months
Sodium Sulfite	12 months	3 to 6 months
Turbidity	12 months	12 months from expiration date
Deionized Water	24 months	Hours, check before use for calibration
Ammonium	12 months	3 to 6 months
Chloride	12 months	3 to 6 months
Nitrate	12 months	3 to 6 months

Potential Interferents

pH
Sodium salts

Dissolved Oxygen
Temperature, atmospheric pressure, salinity, chlorinity

Ammonium
Cesium, Potassium, Thallium, pH, Silver, Lithium, Sodium

Nitrate
Perchlorate, Iodide, Chlorate, Cyanide, Bromide, Nitrite, Hydrogen Sulfide (bisulfite), Hydrogen Carbonate
(bicarbonate), Carbonate, Chloride, Dihydrogen Phosphate, Hydrogen Phosphate, Phosphate, Acetate, Fluoride, Sulfate

Conductivity
Temperature

ORP
Ions that are stronger reducing agents than hydrogen or platinum, e.g., chromium, vanadium, titanium, etc.

Chloride
Hydroxide, Ammonia, Thiosulfate, Bromide, Sulfide, Iodide, Cyanide

BGA-PC, BGA-PE, Chlorophyll a, Rhodamine WT
Turbidity

RDO Cap Chemical Incompatibility



The following chemicals will damage the RDO sensing element.

- Alcohols > 5%
- Hydrogen peroxide > 3%
- Sodium hypochlorite (commercial bleach) > 3%
- Gaseous sulfur dioxide
- Gaseous chlorine
- Do not use in organic solvents (e.g., acetone, chloroform, methylene chloride, etc.), which may destroy the sensing element

Conductivity/Temperature Sensor



Soaking the Conductivity/Temperature sensor in vinegar for longer than one hour can cause serious damage.

Ammonium, Chloride, and Nitrate Interferent Concentrations

Ammonium

The table below lists concentrations of possible interfering ions that cause 10% error at various levels (in ppm) of NH_4^+.

Ion	100 ppm NH_4^+	10 ppm NH_4^+	1 ppm NH_4^+
Celsium (Cs^+)	100	10	1
Potassium (K^+)	270	27	2.7
Thallium (Tl^+)	3100	310	31
pH (H^+)	pH 1.6	pH 2.6	pH 3.6
Silver (Ag^+)	270,000	27,000	2,700
Lithium (Li^+)	35,000	3,500	350
Sodium (Na^+)	11,100	1,100	110

Chloride

The table below lists concentrations of possible interfering ions that cause 10% error at various levels (in ppm) of Cl^-.

Ion	100 ppm Cl^-	10 ppm Cl^-	1 ppm Cl^-
Hydroxide (OH^-)	3,840	384	38.4
Ammonia (NH_3)	6	0.6	0.06
Thiosulfate ($S_2O_3^{2-}$)	3	0.3	0.03
Bromide (Br^-)	0.68	0.068	6.8 x 10-3
Sulfide (S^{2-})	9 x 10-5	9 x 10-6	9 x 10-7
Iodide (I^-)	1.8 x 10-4	1.8 x 10-5	1.8 x 10-6
Cyanide (CN^-)	1.5 x 10-5	1.5 x 10-6	1.5 x 10-7

Nitrate

The table below lists concentrations of possible interfering ions that cause 10% error at various levels (in ppm) of $N0_3^-$.

Ion	100 ppm NO_3^-	10 ppm NO_3^-	1 ppm NO_3^-
Perchlorate (ClO_4^-)	7 x 10-2	7 x 10-3	7 x 10-4
Iodide (I^-)	4	0.4	0.04
Chlorate (ClO_3^-)	30	3	0.3
Cyanide (CN^-)	20	2	0.2
Bromide (Br^-)	400	40	4
Nitrite (NO_2^-)	230	23	2
Hydrogen Sulfide (HS^-)	230	23	2

Bicarbonate (HCO_3^-)	440	440	44
Carbonate (CO_3^{2-})	8,600	860	86
Chloride (Cl^-)	7,600	760	76
Dihydrogen Phosphate ($H_2PO_4^-$)	34,640	3,464	346
Hydrogen Phosphate (HPO_4^{2-})	34,300	3,430	343
Phosphate (PO_4^{3-})	33,900	3,390	339
Acetate (OAc^-)	104,200	10,420	1,042
Fluoride (F^-)	81,400	8,140	814
Sulfate (SO_4^{2-})	685,700	68,570	6,857

Barometric Pressure Sensor Specifications

Accuracy	±1.0 mbar
Range	300 to 1,100 mbar
Resolution	0.1 mbar
Sensor Type	Fixed
Response Time	T63<1s, T90<1s, T95<1s
Units of Measure	psi, kPa, bar, mbar, mmHg, inHg
Methodology	Silicon strain gauge

Conductivity Sensor Specifications

Accuracy	±0.5% of reading plus 1 µS/cm from 0 to 100,000 µS/cm;±1.0% of reading from 100,000 to 200,000 µS/cm; ±2% of reading from 200,000 to 350,000 µS/cm
Range	0 to 350,000 µS/cm
Resolution	0.1 µS/cm
Sensor Type	Removeable
Response Time	T63<1s, T90<3s, T95<5s
Units of Measure	Actual conductivity: µS/cm, mS/cm Specific conductivity: µS/cm, mS/cm Salinity: PSU Total dissolved solids: ppt, ppm Resistivity: Ohms-cm Density: g/cm3
Methodology	Std. Methods 2510, EPA 120.1

*Accuracy at calibration points. For greatest accuracy over instrument life, keep the conductivity cell submersed in water for 24-48 hours prior to calibration and deployment.

Total Dissolved Solids

TDS is derived from conductivity and temperature.

Range	0 to 350 ppt
Resolution	0.1 ppt
Units of Measure	ppt, ppm

Salinity

TDS is derived from conductivity and temperature.

Range	0 to 350 PSU
Resolution	0.1 PSU
Units of Measure	PSU, ppt
Methodology	Std. Methods 2520A

Dissolved Oxygen RDO Sensor Specifications

Accuracy	±0.1 mg/L from 0 to 8 mg/L ±2% of reading from 20 to 50 mg/L
Range	0 to 20 mg/L 20 to 60 mg/L
Resolution	0.01 mg/L
Sensor Type	Removable with replaceable RDO-X Cap
Response Time	RDO-X Cap: T63<15s, T90<45s, T95<60s Fast Cap: T63<3s, T90<30s, T95<45s
Units of Measure	mg/L, % saturation, ppm
Methodology	EPA-approved In-Situ Methods (under the Alternate Test Procedure process): 1002-8-2009, 1003-8-2009, 1004-8-2009

Level, Depth, Pressure Sensor Specifications

Accuracy	Typical ±0.1% full scale (FS)
Range	Non-vented or Vented 9.0 m (30 ft) - Burst: 27 m (90 ft) 30 m (100 ft) - Burst: 40 m (130 ft) 76 m (250 ft) - Burst: 107 m (350 ft) 200 m (650 ft) - Burst: 229 m (750 ft)
Resolution	±0.01% FS or better
Sensor Type	Fixed
Response Time	T63<1s, T90<1s, T95<1s

Units of Measure	Pressure: psi, kPa, bar, mbar, mmHg, inHg, cmH2O, inH2O Level: mm, cm, m, in, ft, cmH2O, inH2O
Methodology	Piezoresistive; ceramic

*Typical performance across full temperature and pressure calibrated range. Typical is defined as all values within 1 standard deviation.

ORP Sensor Specifications

Accuracy	±5.0 mV @ 25° C
Range	±1,400 mV
Resolution	0.1 mV
Sensor Type	Replaceable pH/ORP combo sensor
Response Time**	T63<3s, T90<15s, T95<30s
Units of Measure	mV
Methodology	Std. Methods 2580

*Accuracy from standard at 25° C.
**At thermal equilibrium immediately following calibration, measuring from air to +400 mV

pH Sensor Specifications

Accuracy	±0.1 pH units or better
Range	0 to 14 pH units
Resolution	0.01 pH unit
Sensor Type	Replaceable pH/ORP combo sensor
Response Time**	T63<1s, T90<2s, T95<3s
Units of Measure	pH units
Methodology	Std. Methods 4500-H+, EPA 150.2

*At thermal equilibrium.

Temperature Sensor Specifications

Accuracy	±0.1° C
Range	-5 to 50° C (23 to 122° F)
Resolution	0.01° C
Sensor Type	Replaceable
Response Time**	T63<2s, T90<15s, T95<30s

Units of Measure	° C, ° F
Methodology	EPA 170.1

Sensor only, when transferring from air to ambient water temperature. Typical system response time with all sensors and restrictor installed: T63<30s; T90<3.5m; T95,7.5m

Turbidity Sensor Specifications

Accuracy	±2% of reading or ±0.5 NTU or FNU, whichever is greater
Range	0 to 4,000 NTU
Resolution	0.01 NTU (0 to 1,000 NTU) 0.1 NTU (1,000 to 4,000 NTU)
Sensor Type	Replaceable
Response Time**	T63<1s, T90<1s, T95<1s
Units of Measure	NTU, FNU
Methodology	ISO 7027

Total Suspended Solids

TSS is derived from turbidity.

Range	0 to 1,500 mg/L
Resolution	0.1 mg/L
Units of Measure	ppt, mg/L

User-defined reference.

Ammonium Sensor Specifications

Accuracy	±10% or ± 2 mg/L, whichever is greater
Max Depth	25 m, 30 PSI
Range	0-10,000 mg/L as N
Resolution	0.01 mg/L
Sensor Type	Removable
Response Time*	T90 < 10sec, T95 < 30sec
Units of Measure	mg/L, ppm, mV
Methodology	Std. Methods 4500-NH_3D, EPA 350.3

*Between calibration points.

Ammonia (Unionized Ammonia and Total Ammonia)

Ammonia is derived from ammonium, pH and salinity. pH sensor and conductivity/temperature sensor required.

Range	0 to 10,000 mg/L
Resolution	0.01 mg/L
Units of Measure	mg/L, ppm

Chloride Sensor Specifications

Accuracy	±10% or ±2 mg/L, w.i.g.*
Range	0-190,000 mg/L - CL-
Resolution	0.01 mg/L
Sensor Type	Removable
Response Time*	T90 < 10sec, T95 < 30sec
Units of Measure	mg/L, ppm, mV
Methodology	Std. Methods 4500-Cl-D

* Between calibration points.

Nitrate Sensor Specifications

Accuracy	±10% or ±2 mg/L, w.i.g.*
Max Depth	25 m, 30 PSI
Range	0-50,000 mg/L as N
Resolution	0.01 mg/L
Sensor Type	Removable
Response Time*	T90 < 10sec, T95 < 30sec
Units of Measure	mg/L, ppm, mV
Methodology	Std. Methods 4500-NO3D

* Between calibration points.

Chlorophyll a Sensor Specifications

Linearity	R2 > 0.999 for serial dilutions of 0-1000 µg/L Chl a in MeOH
Max Depth	200 m

Range	0-100 RFU 0-1000 µg/L Chl a in MeoH
Resolution	.001 RFU .01 µg/L Chl a
Sensor Type	Removable
Response Time*	T63<1s, T90<1s, T95<1s
Units of Measure	Concentration: µg/L Fluorescence: RFU
Excitation Wavelength (nominal)	430 nm
Detection Wavelength	675 nm to 750 nm

BGA-PC Sensor Specifications

Linearity	R2 > 0.999 for serial dilutions of PC standards from 0-1000 µg/L PC
Max Depth	200 m
Range	0-100 RFU 0-1000 µg/L PC
Resolution	.001 RFU .01 µg/L PC
Sensor Type	Removable
Response Time*	T63<1s, T90<1s, T95<1s
Units of Measure	Concentration: µg/L Fluorescence: RFU
Excitation Wavelength (nominal)	590 nm
Detection Wavelength	640 nm to 690 nm

BGA-PE Sensor Specifications

Linearity	R2 > 0.999 for serial dilutions of PE standards from 0-1000 µg/L PE
Max Depth	200 m
Range	0-100 RFU 0-1000 µg/L PE
Resolution	.001 RFU .01 µg/L PE
Sensor Type	Removable
Response Time*	T63<1s, T90<1s, T95<1s

Units of Measure	Concentration: µg/L Fluorescence: RFU
Excitation Wavelength	498 nm
Detection Wavelength	575 nm to 625 nm

Rhodamine WT Sensor Specifications

Linearity	R2 > 0.999 for serial dilutions of RWT (Rhodamine Water Tracer) standards from 0-1000 µg/L
Max Depth	200 m
Range	0-100 RFU 0-1000 µg/L
Resolution	.001 RFU .01 µg/
Sensor Type	Removable
Response Time*	T63<1s, T90<1s, T95<1s
Units of Measure	Concentration: µg/L Fluorescence: RFU
Excitation Wavelength (nominal)	530 nm
Detection Wavelength	580 nm to 660 nm

Fluorescein WT Sensor Specifications

Linearity	R2 > 0.999 for serial dilutions of FWT (Fluorescein Water Tracer) standards from 0-500 µg/L
Max Depth	200 m
Range	0-100 RFU 0-500 µg/L
Resolution	.001 RFU .005 µg/L
Sensor Type	Removable
Response Time*	T63<1s, T90<1s, T95<1s
Units of Measure	Concentration: µg/L Fluorescence: RFU
Excitation Wavelength (nominal)	462 nm
Detection Wavelength	525 nm to 570 nm

FDOM Sensor Specifications

Linearity	R2 > 0.999 for serial dilutions of Quinine Sulfate from 0-3000 µg/L
Max Depth	200 m
Range	0-100 RFU 0-3000 µg/L
Resolution	.001 RFU .03 µg/L
Sensor Type	Removable
Response Time*	T63<1s, T90<1s, T95<1s
Units of Measure	Concentration: µg/L Fluorescence: RFU
Excitation Wavelength (nominal)	375 nm
Detection Wavelength	455 nm to 530 nm

Crude Oil Sensor Specifications

Linearity	R2 > 0.999 for serial dilutions of PTSA from 0-3000 µg/L
Max Depth	200 m
Range	0-100 RFU 0-3000 µg/L
Resolution	.001 RFU .03 µg/L
Sensor Type	Removable
Response Time*	T63<1s, T90<1s, T95<1s
Units of Measure	Concentration: µg/L Fluorescence: RFU
Excitation Wavelength (nominal)	365 nm
Detection Wavelength	430 nm to 505 nm

Warranty	2 year - Sonde, RDO and sensor cap, temperature/conductivity, temperature only, turbidity (excluding pH/ORP) 1 year - pH/ORP, chloride ISE, accessories 90 Days - Nitrate and Ammonium ISE sensors Other: see warranty policy (www.in-situ.com/warranty)
Notes	Specifications are subject to change without notice. Android is a trademark of Google, Inc. Bluetooth is a trademark of Bluetooth SIG, Inc. Delrin and Tefzel are trademarks of E.I. du Pont de Nemours & Co. Santoprene is a trademark of ExxonMobile. Inconel is a trademark of Special Metals Corporation. Viton is a registered trademark of DuPont Performance Elastomers L.L.C.

Required Accessories

Communication Device

You can use a communication device to calibrate, configure and deploy the Aqua TROLL 600.



Wireless TROLL Com

Provides power to the Aqua TROLL 600 to extend battery life.

Configure and deploy with a Bluetooth-endabled Android device.

Connects the Aqua TROLL 600 to a PC via USB.

Cable



Rugged Twist-Lock Cable

Connects the Aqua TROLL 600 to a Wireless TROLL Com, USB TROLL Com or VuLink.

Vented or non-vented.

Sensors



Available Sensors

1 Temperature
2 Conductivity/temperature
3 pH/ORP
4 RDO
5 Turbidity
6 Ammonium
7 Chloride
8 Nitrate
9 Chlorophyll a
10 BGA-PC
11 BGA-PE
12 Rhodamine WT
13 Fuorescein WT
14 FDOM
15 Crude Oil

Software



Win-Situ 5 Software for PC

Calibrate, configure and take readings with the Aqua TROLL 600 from a PC.

Download it from www.in-situ.com.



VuSitu Mobile App

Calibrate, configure and deploy the Aqua TROLL 600 from a Bluetooth-enabled Android device.

Get it at play.google.com.

Telemetry



VuLink

Power Aqua TROLL 600 in remote-monitoring applications

Calibrate, configure, and deploy the Aqua TROLL 600.

Send data to HydroVu or an external FTP Server

System Components

Base Unit Components

Component	Part Number
RDO Sensor - includes RDO-X Cap	0063450
Combination pH/ORP Sensor	0063470
Turbidity Sensor	0063480
Combination Conductivity/Temperature Sensor or standalone Temperature Sensor	0063460, 0063490
Alkaline Batteries (2)	0042020
Dual Stainless Steel Restrictor/Storage Chamber	0079820
Sensor Port Plugs (2)	0063510
Rubber Bumpers (2)	0079880
Wiper or Wiper Port Plug	0063500, 0064630
Additional Sensors	
Ammonium Sensor	0033700
Nitrate Sensor	0033710
Chloride Sensor	0033720
Chlorophyll A Sensor	0038900
Phycocyanin (BGA-PC) Sensor	0038920
Phycoerythrin (BGA-PE) Sensor	0038930
Rhodamine WT Sensor	0038890
Fluorescein WT Sensor	0096050
Crude Oil Sensor	0096060
Fluorescent Dissolved Organic Matter (FDOM) Sensor	0096070
Communications	
Wireless TROLL Com for Android	0031240
Mobile Device for Android	0064860
TROLL Com RS-232 Cable Connect	0056140
TROLL Com USB Cable Connect	0052500
TROLL Com RS-232 Direct Connect	0056150
TROLL Com USB Direct Connect	0052510

Cable	
Stripped-and-tinned Cable with male connector	0053310
Twist-lock Bulkhead Connector	0053240
Twist-lock Backshell/Hanger, Titanium	0051480
Cable Extender	0051490
Large Desiccant (titanium connector)	0051810
Large Desiccant (ABS connector)	0053550
Small Desiccant (3 pack) - storage desiccant	0052230
Desiccant Refill Kit for Large or Outboard Desiccant	0029140

Calibration and Maintenance	
RDO Classic Cap Replacement Kit	0079790
pH/ORP Replacement Reference Junction Kit	0078990
Wiper Brush Kit	0079810
Maintenance Kit	0078940
Copper Antifouling Guard	0076100
Quick-Cal Solution for calibrating DO, Cond., pH & ORP	0033250
Dissolved Oxygen Calibration Kit	0032110
D.O. Field Calibration Kit	0080830
Conductivity Calibration Kit (Full)	0032090
Conductivity Calibration Kit (Low)	0032630
Conductivity Calibration Kit (High)	0032640
pH Calibration Kit	0032080
pH/ORP Calibration Kit	0032120
pH Storage Solution	0065370
Individual Calibration Solutions	See website
Ammonium Calibration Kit (includes 1 liter each: 14 ppm, 140 ppm, 1400 ppm, DI water)	0032140
Chloride Calibration Kit (includes 1 liter each: 35.5 ppm, 355 ppm, 3545 ppm, DI water)	0032150
Nitrate Calibration Kit (includes 1 liter each: 14 ppm, 140 ppm, 1400 ppm, DI water)	0032130
Fluorescein WT Solid State RFU Calibrator	0104290
FDOM Solid State RFU Calibrator	0104300
Crude OIl Solid State RFU Calibrator	0104310

Low-Flow	
Complete Low-Flow Kit (includes flow cell with fittings and stake, base plate, documentation)	0079790
Flow Cell Kit	0078990
Flow Cell Base Plate	0079810
Fittings Kit	0032130
Pelican Case with Foam Insert	0066860

RuggedCable System

RuggedCable Systems are custom-built, durable, direct-read cables that include the following items:

- Titanium twist-lock connectors for quick, reliable connections to the instrument, desiccant, and communication cable
- Metal shield beneath the cable jacket to prevent electrical interferences
- Kellems grip for secure instrument deployment
- Small desiccant for vented systems (for storage only)

Non-vented cables are marked with VF, which means vent free.

Vented or Non-Vented Cable

Vented cable is used with vented pressure sensors to produce gauged measurements. The cable vent tube ensures that atmospheric pressure is applied to the back of the sensor diaphragm.

Non-vented cable is used with non-vented instruments for absolute measurements. Compensate absolute measurements by using a BaroTROLL Instrument and Win-Situ Baro Merge Software.

Vented cable is shipped with a small desiccant to protect against condensation. Larger desiccants are necessary for deployment.

Jacket Options

Tefzel (vented) or thermoplastic polyurethane (TPU, vented or non-vented)

Customizable Cable Lengths

Cables can be ordered up to 1,219 m (4,000 ft).

Cable Termination

Cables can be ordered with a twist-lock termination (female connector) on both ends that connect to the instrument, the TROLL Com Communication Device, desiccant, and other accessories.

Cables can also be ordered with stripped-and-tinned termination for wiring to a data logger or controller using SDI-12, analog (4-20 mA), or Modbus communication protocol.



1	RuggedCable System with female to female connectors
2	Stripped-and-tinned RuggedCable System with female connector
3	Stripped-and-tinned RuggedCable System with male connector (short length that converts a cable with a twist-lock connector to a stripped-and-tinned cable)

Aqua TROLL 600 Quickstart Guide



Box Contents

1 Documentation and software
2 Wiper motor and brush/wiper
3 Aqua TROLL 600 sonde
4 Water quality sensors (2 of 4)
5 Water quality sensors (2 of 4)
6 RDO sensor cap
7 Accessory supplies
8 pH/ORP sensor maintenance supplies
9 Extra sensors
10 D-cell alkaline batteries
11 Instrument tools

Getting Started

1 Install the batteries.



Open the battery compartment.



Install alkaline batteries.



Use Allen wrench to remove and check desiccant color. If pink, replace.



Close battery compartment. LCD screen should activate.

2 Install the wiper motor and sensors.



Remove restrictor.



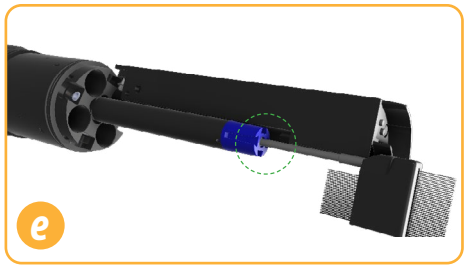
Apply a pea-sized drop of lubricant to O-rings.



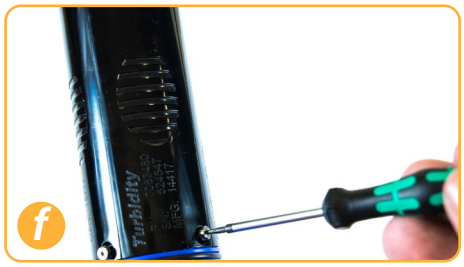
Install wiper motor or port plug into center port.



Apply a pea-sized drop of lubricant to O-rings.



Align sensor with interlock groove in wiper motor and slide sensor into port.



Tighten set-screw at base of each sensor.



Unscrew end cap from restrictor.



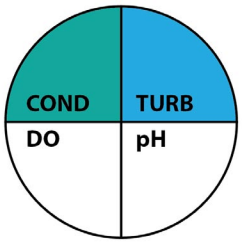
Flip restrictor and install with restrictor holes near center of instrument for calibration.



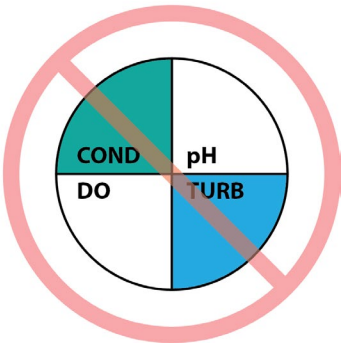
Flip restrictor and replace end cap before deployment.

When using a conductivity sensor and turbidity sensor together, install them side-by-side to maximize performance.

EFFICIENT
SENSOR CONFIGURATION
– END VIEW–



INEFFICIENT
SENSOR CONFIGURATION
– END VIEW–



3 Connect the cable to the instrument.



Remove protective caps from instrument and cable.



Ensure O-ring on instrument connector is clean. Apply vacuum grease to O-ring.



Flat edge inside cable end must align with flat edge on instrument connector.



Hold textured sleeve of cable in one hand and instrument in other. Push and twist until click.

4 Connect the communication device.



If desiccant is present, remove it from cable.



Align TROLL Com connector with cable end. Push and twist until click.

or

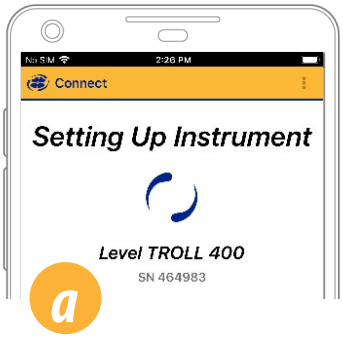


Connect VuSitu directly to instrument. Hold sonde vertically with sensors up. Screen will activate.

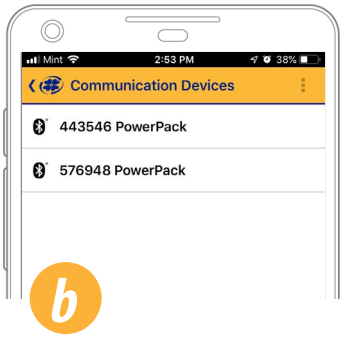
5 Connect to the software.

You must have the VuSitu mobile app to use the instrument with a mobile device. Download VuSitu from the Google Play Store or the Apple App Store.

iOS

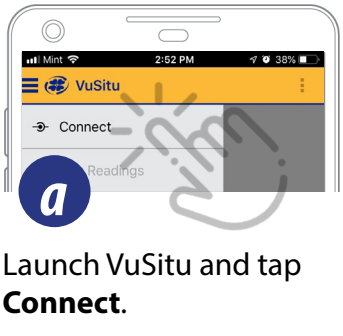


An iOS device automatically connects to the closest In-Situ instrument.



To connect to another instrument, press **Disconnect** and then **Choose or Add Device**. VuSitu displays a list of available connections.

Android



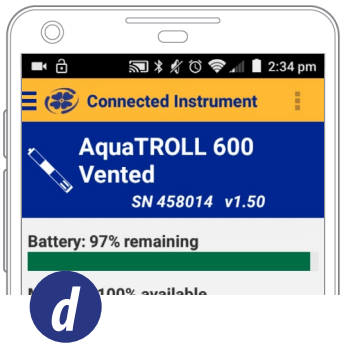
Launch VuSitu and tap **Connect**.



The app locates and displays nearby In-Situ devices.



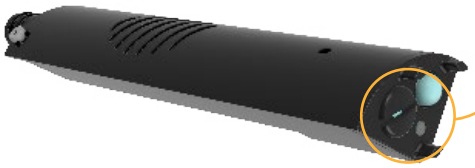
Tap the serial number of the instrument or Wireless TROLL Com.



VuSitu displays the Connected Instrument screen when pairing is complete.

Handling pH and Ion-Selective Electrode Sensors (ISEs)

Salt may accumulate around the reference junctions of the ammonium, chloride, nitrate and pH sensors. Rinse with deionized water to remove any buildup.



Potential salt buildup. Rinse with deionized water if necessary.

Before using the **ISE sensors** for the first time, replace the reference filling solution. Condition the sensors by soaking in calibration standard for 4-24 hours prior to deployment. This step is not necessary for the pH sensor.



1. Unscrew reference junction.
2. Replace reference filling solution.

Using the RDO Sensor and RDO Fast Cap

The wiper can severely reduce the life of the RDO Fast Cap. Wear will vary by application. Verify sensor performance prior to use and replace the Fast Cap if damaged.



Inspect foil prior to each use. If damaged, replace cap.

RDO Fast Cap

Wiper

Ion-Selective Electrode Sensor (ISE) Requirements

ISE sensors require one or more additional sensors to function. See the details below and install the required sensors to use an ISE.

Ammonium Sensor Requirements

Conductivity/ Temperature Sensor



or

Temperature Sensor



To calculate ammonia...

Conductivity/ Temperature Sensor



and

pH Sensor



Chloride, Nitrate, and pH/ORP Sensor Requirements

Conductivity/ Temperature Sensor



or

Temperature Sensor



Do not look directly at the sensor LED or point it at the eyes. Doing so can cause eye damage.

LCD Screen

View instrument status, change settings, start and stop logs via the LCD screen.

Accessing the LCD Menu



Hold the instrument vertically with the sensor end facing up to activate the LCD screen.



Hold instrument horizontally and slowly tap Aqua TROLL 600 logo 3-4 times to view the main menu.



Tilt instrument left or right to scroll through menu options.



Select an item when its background turns black by tapping the instrument once.



You can enable Bluetooth communication directly with the sonde via the Bluetooth menu option.

LCD Status Indicators



1 Port Status

2 Power Status

3 Log Status

4 Connection Status

Possible Port Statuses

Sensors installed

Port plugs installed

Sensor/port error

Possible Power Statuses

Battery level indicator

External power provided

Battery below 10% or Battery error

Possible Log Statuses

Log is Running

Log is Scheduled

Log is Paused

No Log Set Up

Possible Connected Statuses

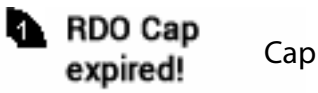
Connected via Bluetooth

Connected via cable

Error Messages



Port(s) empty



Cap expiration

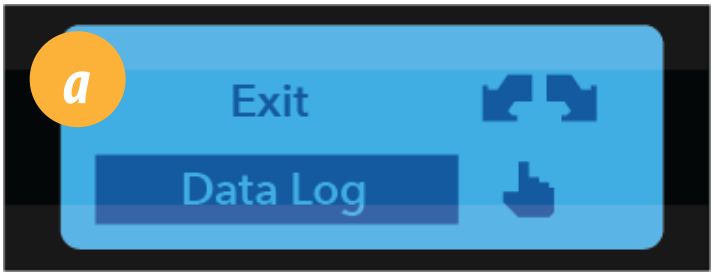
Full-Text Messages

The LCD will display text messages instead of status icons when certain conditions are met. Multiple messages will rotate and display for 3 seconds each.

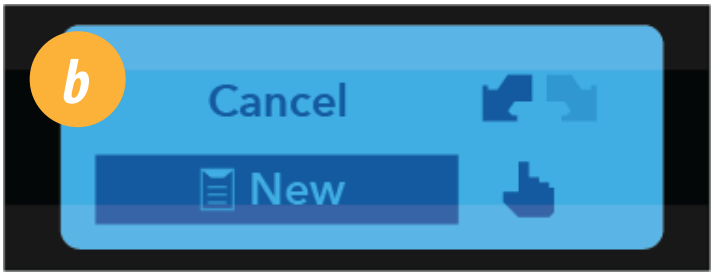
Text Message	Cause and Remedy
Close battery cover	Battery cover is not fully closed. Ensure the battery cover is securely tightened.
Install wiper	Wiper sensor port is open. Install wiper or wiper port plug into center port.
Install sensors	Sensor ports are open. Install sensors or sensor port plugs.
Install temperature	No Temperature or Conductivity/Temperature sensor detected. Install a sensor with Temperature.
Install RDO Cap	RDO Cap not detected on RDO sensor. Install RDO cap.
RDO Cap expired	RDO cap is no longer valid. Install a new RDO Cap.
RDO Cap XXX days	Temporary text message update on the lifespan of the RDO Cap.

Starting a Log with the LCD Menu

The data log menu allows you to create and start a basic linear data log if one doesn't already exist on the instrument.



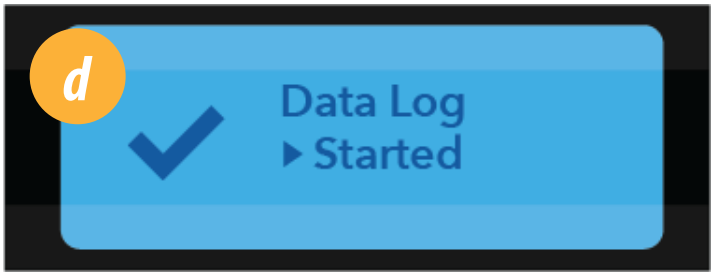
Activate the LCD menu and select **Data Log**.



Choose **New**.



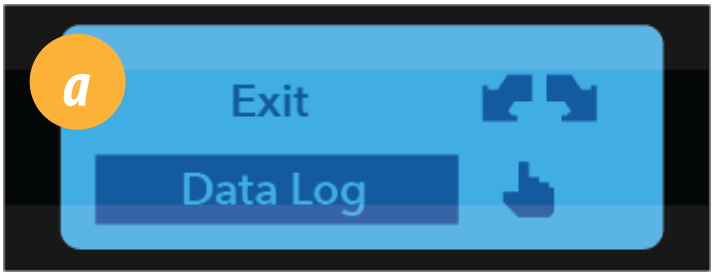
Set the logging interval.



The log starts immediately.

You can't update firmware while a log is running. Stop a log to update the sonde or sensors.

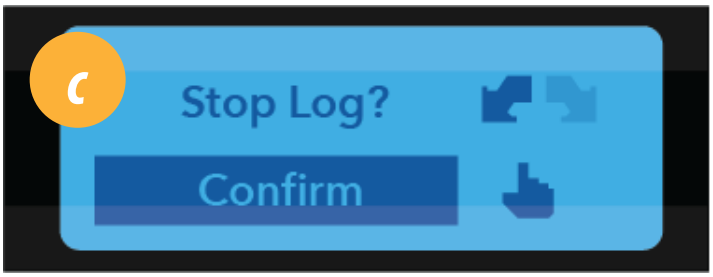
Stopping a Log



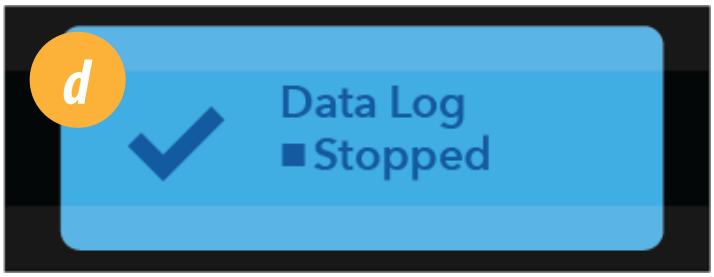
Activate the LCD menu and select **Data Log**.



Choose **Stop**.

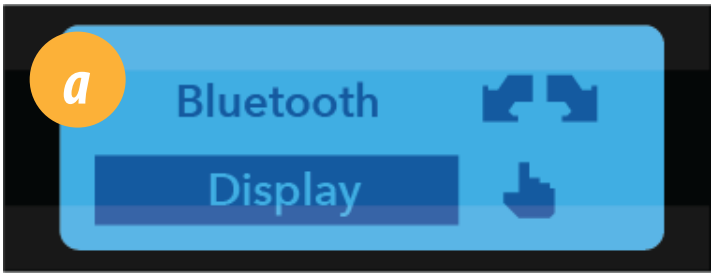


Select **Confirm** to stop the log.



The log stops immediately.

Adjusting the LCD Menu Contrast



Activate the LCD menu and scroll to **Display**. Tap once to select.

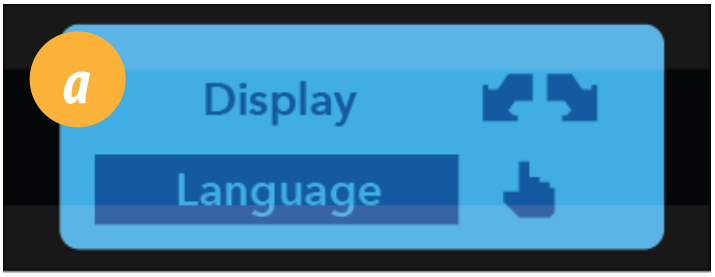


Select **Contrast**.



Tilt the sonde to the left to decrease the contrast. Or, tilt the sonde to the right to increase contrast. Tap the Aqua TROLL 600 logo to set the contrast.

Setting or Changing Menu Language



Access the language menu.



Highlight the desired language and tap.



The LCD screen confirms the new language.

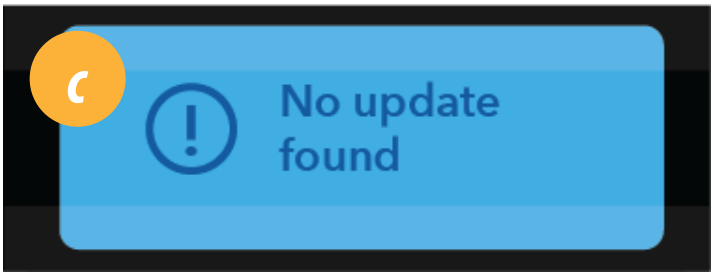
Viewing the Updates Menu



Access the updates menu.



Highlight the desired component to update (Sonde, Sensor 1, 2, 3, or 4).



If the firmware is already up to date, the LCD displays message indicating that an update isn't available. Select **Yes** if an update is available.

If an update is present on the SD card, the screen will indicate the previous firmware version, a right-facing arrow, and the new version of the firmware.

Micro SD Card

The Aqua TROLL 600 uses a micro SD card for data storage and updating sonde firmware. You can remove the SD card and replace it with another for data download, or use the same card. An SD card is not required to log data.

Removing the Micro SD Card

The micro SD card is housed in a slot near the positive battery terminal and the twist-lock connector.

1 Remove the battery cover from the end of the instrument.

2 Push the micro SD card in towards the instrument to release the card.

3 Remove the card from the slot.

4 To reinstall the card, note the card position diagram in the finger slot. Push the card into the slot until you hear a click.

Downloading and Deleting Data from the Micro SD Card

1 Remove card from the sonde and insert it into a micro SD card adapter.

2 Insert the adapter into a PC or laptop.

3 Open the micro SD card using the file explorer.

4 Open the folder titled "Serial Number.LOG." For example, "424690.LOG."



Logs are named by date and then number. For example, a log started on November 12, 2015 would be named "15111200.CSV" - 15 is the year, 11 is the month, 12 is the day, and 00 is the log number. If multiple logs are recorded on the same day the last number will increase by one for each consecutive log.

5 Select the logs you wish to download and move them to the destination.

6 Select the logs you wish to delete and press Delete on the keyboard. Deleted logs cannot be recovered.

Updating Firmware

1 Download the firmware update files to your computer.

2 Remove the SD card from the unit and insert it into your computer.



You may need a micro SD card adapter to connect the SD card to your computer. One is included with your Aqua TROLL 600, but any micro SD card adapter can be used.

3 Copy the firmware update files into the ISI.FW file on the SD card.

4 Install the SD card into the instrument and install the battery cover.

5 Turn on the LCD screen by inverting the sonde so the sensor end faces up.

6 Access the instrument menu by tapping the Aqua TROLL 600 logo on the yellow label three times. For more information on accessing menus, see "LCD Screen."

7 Scroll to Updates by tilting the instrument. Access the Updates menu by tapping the Aqua TROLL 600

8 logo once.

9 Scroll to Sonde by tilting the instrument. Tap the Aqua TROLL 600 logo once.

10 The LCD screen will display the current firmware version on the left, then an arrow, and the new firmware version on the right.

11 Scroll to Yes by tilting the instrument. Tap the Aqua TROLL 600 logo once.

12 The LCD screen will display icons while updating. Once the update is complete the Aqua TROLL 600 and LCD screen will restart.

Replacing Desiccant

A replaceable desiccant capsule prevents moisture from damaging the instrument and batteries. Check the capsule periodically. A pink color indicates expired/exhausted desiccant.



Remove the battery cover.



Remove the wrench from the back of the battery compartment.



Insert the wrench into the hole in the back of the battery compartment and push the desiccant capsule out.



Insert a new capsule. Replace the wrench and battery cover.

Calibrating Sensors

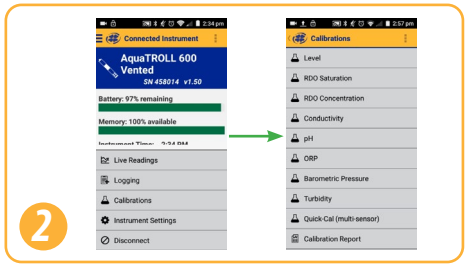
Solution-Based Calibration

Use the solution-based procedure described below to calibrate all sensors except RDO. You will need the following items.

- Calibration standard, or multiple standards for multi-point calibrations
- Wireless TROLL Com connected to the Aqua TROLL 600
- Bluetooth-enabled mobile device



Hold the sonde upright to activate the LCD screen. Pair the sonde with the VuSitu app.



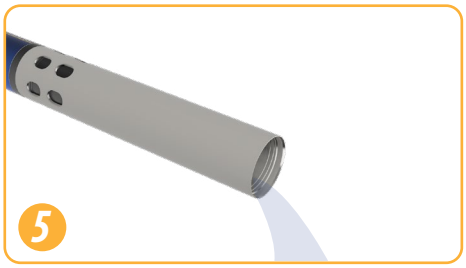
In VuSitu, click Calibrations from the Connected Instrument screen and choose sensor to calibrate.



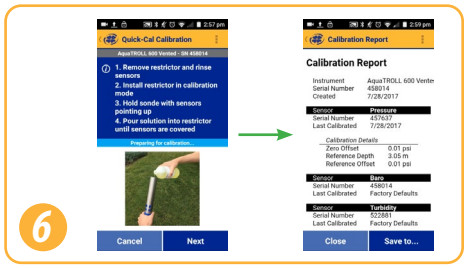
Remove cap from instrument and pour 10-20 ml of DI water into restrictor.



Gently shake the sonde in a circular motion to rinse the inside of restrictor and sensors.



Discard the DI water and repeat rinsing procedure two more times with 10-20 ml of your first calibration standard.



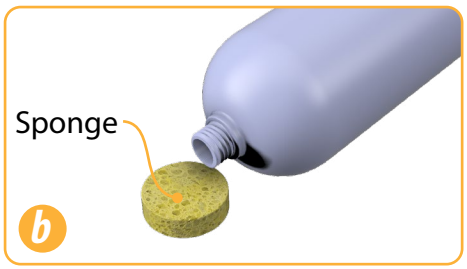
Follow the instructions in VuSitu to perform the calibration.

RDO 100% Saturation Calibration: Water Saturated Air

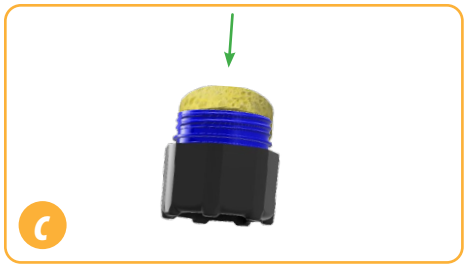
Use the procedure below to calibrate the Aqua TROLL 600 RDO sensor, or see the next section for an alternative method.



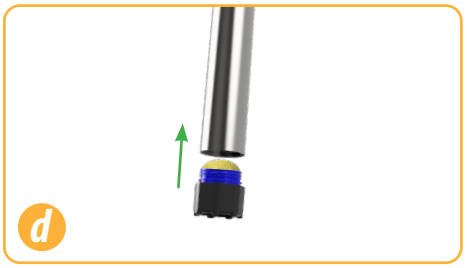
Place the restrictor in calibration mode (holes near center of instrument).



Saturate a small sponge with water.



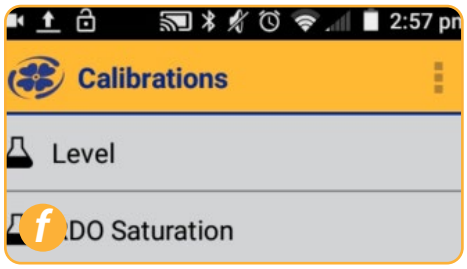
Place the sponge on the restrictor cap.



Loosely install the end cap, keeping the sensor face dry and allowing for air flow.

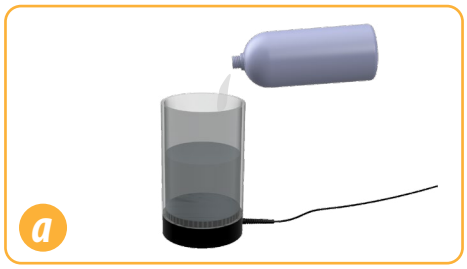


Leave sponge in restrictor for five minutes.



Follow the instructions in VuSitu to finish calibration.

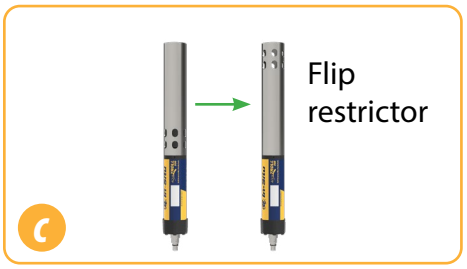
RDO 100% Saturation Calibration: Saturation Bubbler



Fill a 100% saturation bubbler two-thirds with tap water.



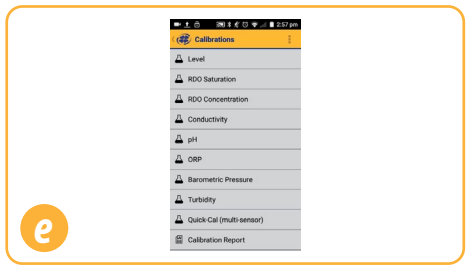
Turn on bubbler and allow 5-10 minutes for 100% saturation.



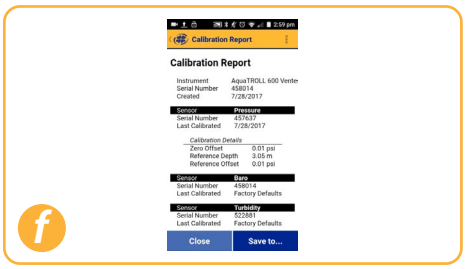
Put sonde into deployment mode by flipping restrictor 180 degrees.



Place sonde into bubbler.



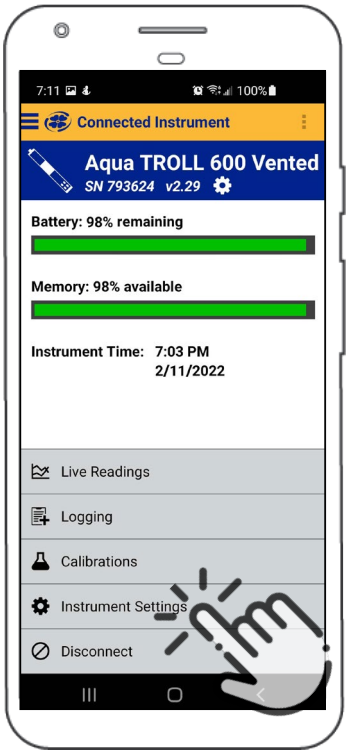
Open the VuSitu mobile app and tap Calibrations > RDO Saturation.



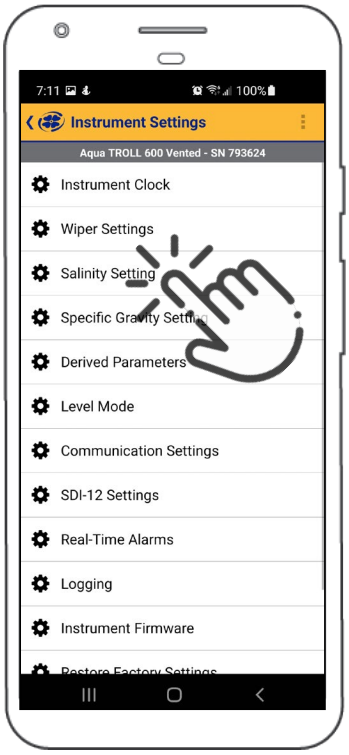
Follow instructions in VuSitu to finish calibration.

RDO Salinity Setting

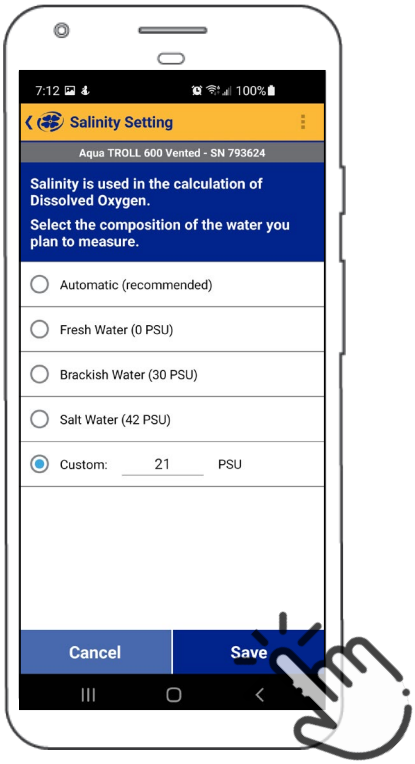
The Aqua TROLL 600 includes automatic salinity compensation. This feature requires a conductivity sensor and RDO sensor. With both sensors installed, the sonde uses salinity compensation by default. To change the compensation value, follow these steps:



Select **Instrument Settings** from the menu at the bottom of the screen.



From the Instrument Settings menu, select **Salinity Setting**.



Enter your desired salinity compensation setting and press **Save**.

Turbidity Sensor Calibration

You must calibrate the turbidity sensor with In-Situ's turbidity standard, or formazine. The app may not automatically detect the formazine concentration. Instead, a field will appear in which you can enter the appropriate value. Select **Set User Defined** to begin calibrating with the new value. If you are using an In-Situ standard and the app does not automatically detect it, perform the sensor cleaning and maintenance procedure, then select **Retry Auto Detect**.

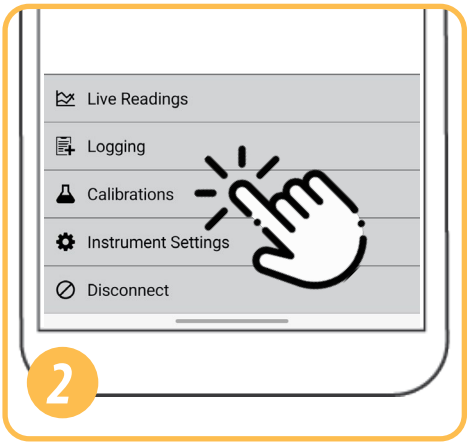
Batch Calibrating Sensors in VuSitu

Different Sensor Types (Quick Cal Solution)

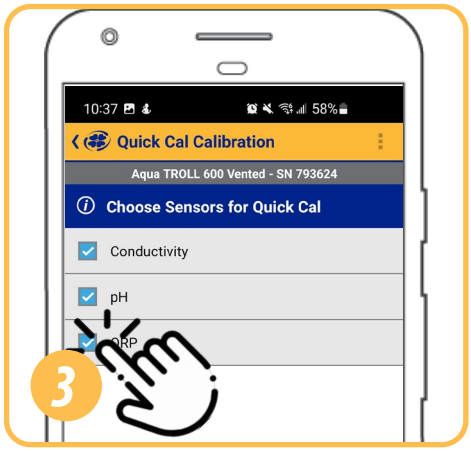
Use Quick Cal standard to calibrate conductivity, pH, and ORP with a single solution. Quick Cal solution can also be used for 100% RDO Saturation calibration. To calibrate multiple sensors of the same type, follow the instructions on the next page.



Install the restrictor in calibration mode (with holes closest to the instrument body).



In VuSitu, click **Calibrations** from the Connected Instrument screen. Choose **Quick Cal** from the menu.



Select sensors to calibrate.



Set up the calibration. Make sure that all sensors are completely submerged.



When all sensors have stabilized, tap **Accept**. Review the calibration report for the completed sensors.



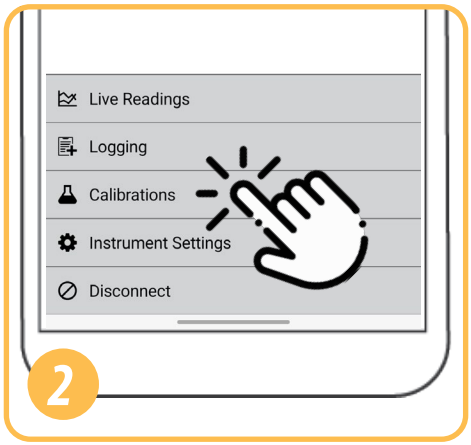
Flip the restrictor back into deployment mode and install the end cap.

Multiple Sensors of the Same Type

For some parameters (pH, ORP, RDO, turbidity, and conductivity), you can calibrate multiple sensors of the same type together. Use this feature when you need to batch calibrate a group of sensors prior to field deployment.



Install the sensors to calibrate. (pH/ORP sensors also require a temperature sensor.) Install the restrictor in calibration mode.



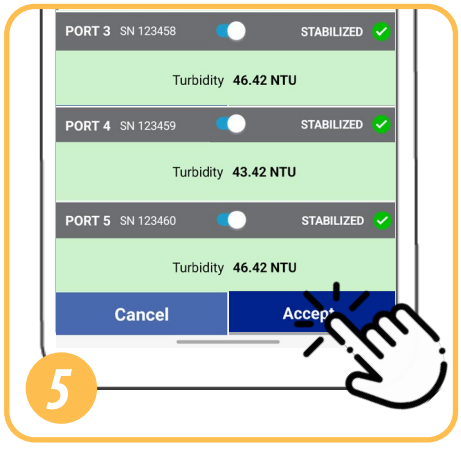
In VuSitu, click **Calibrations** from the Connected Instrument screen. Choose a calibration to perform.



Set up the calibration. Make sure that all sensors are completely submerged or in the same calibration environment.



Wait for calibrations to complete. If one sensor isn't stablilizing, use the toggle switch to turn that sensor off and continue calibrating the others.



When all sensors have stabilized, tap **Accept**. Review the calibration report for the completed sensors.



Remove sensors and install them in the instruments they will be deployed in.

Calibration Frequency Recommendations

In-Situ sensors are factory calibrated across the entire range of each sensor, and thus achieve a very high degree of accuracy and stability for extended periods of time without user calibration. In-Situ recommends inserting the instrument into a known calibration standard to check the accuracy of a sensor prior to performing any user calibration if you suspect drift, unless a user calibration is required by a standard operating procedure.

Sensor	Recommended User Calibration Frequency	Recommended Factory Calibration Frequency	Notes
Conductivity	Only when required by user protocol	12 months	K-cell value: 0.7 to 1.3
Conductivity + Temperature	Only when required by user protocol	12 months	K-cell value: 0.7 to 1.3
pH	10 to 12 weeks or as required by user protocol or site conditions	12 months	Single point: Theoretical mV ±30 mV 2- or 3-point Slope: -66 to 50 mV/pH 2- or 3-point Offset: ±30mV at pH 7
ORP	10 to 12 weeks or as required by user protocol or site conditions	12 months	Offset: ±30 mV
RDO	12 months or as required by user protocol	12 months	2-point Slope: 0.7 to 1.3 2-point Offset: ±0.3 mg/L
Temperature	Only when required by user protocol	Only when required by user protocol	Offset: ±0.5
Turbidity	Only when required by user protocol	12 months	Slope: 0.7 to 1.3
Pressure/Depth	Only when required by user protocol	Only when required by user protocol	<2 times the full scale accuracy specification
Barometer	Only when required by user protocol	Only when required by user protocol	<2 times the full scale accuracy specification
Ammonium	Monthly	N/A	Slope > 20 mV/decade
Chloride	Monthly	N/A	Slope < -20 mV/decade
Nitrate	Monthly	N/A	Slope < -20 mV/decade

Chlorophyll a	Only when required by user protocol	12 months	
BGA-PC	Only when required by user protocol	12 months	
BGA-PE	Only when required by user protocol	12 months	
Rhodamine WT	Only when required by user protocol	12 months	
Fluorescein WT	Only when required by user protocol	12 months	
FDOM	Only when required by user protocol	12 months	
Crude Oil	Only when required by user protocol	12 months	

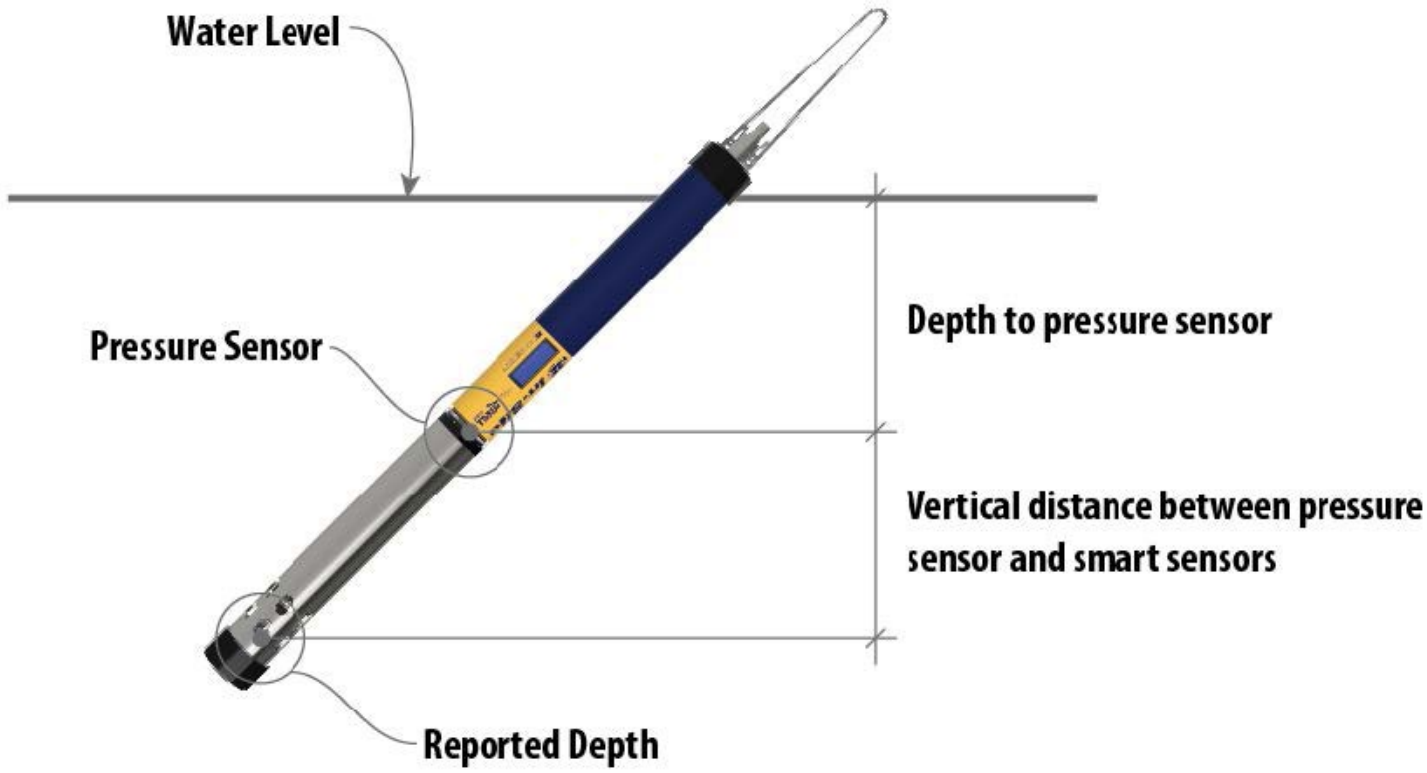
Factory Calibration

Factory calibration includes a thorough cleaning, full functionality check and sensor adjustments to all applicable sensors over the entire calibrated temperature range. We recommend a factory calibration every 12 months or when the unit appears to drift significantly.

Zeroing the Depth Sensor

The Aqua TROLL 600 uses its pressure reading and specific gravity value to calculate depth. The pressure sensor is located at the center of the instrument, but depth is reported at the smart sensor faces. An embedded gyroscope compensates for the distance between these sensors and allows the sonde to be deployed in any orientation (vertical, horizontal, angled).

Do not zero the pressure sensor. Erroneous readings will result.



Error Code	Error Description	Recommended Actions
UC[0]	User Calibration (UC) Expired	1.) Perform a user calibration on the sensor in a known calibration standard 2.) Follow individual sensor instructions or user SOPs for calibration.
FC[0]	Factory Calibration (FC) Expired	Call (800-446-7488) or contact In-Situ Technical Support (support@in-situ.com). Send the instrument back to In-Situ for factory calibration

OL	Sensor Office (OL) and no longer communicating with the instrument	1.) Remove sensor and check for water in the connection port. Dry sensor and sonde connector. Reinstall sensors. 2.) Remove two sensors and reinstall in separate port. 3.) Call (800-446-7488) or contact In-Situ Technical Support (support@in-situ.com).
WU[0]	Wiper Error - wiper is not turning correctly or interfering with sensor performance	1.) Inspect wiper to ensure surface is free of debris and the wiper is spinning correctly. 2.) Remove wiper brush and install a new brush holder with new brushes. 3.) Remove the wiper and check for water in the connection port. Dry the wiper port and the sonde connector. Reinstall wiper. 3.) Call (800-446-7488) or contact In-Situ Technical Support (support@in-situ.com).
ERR[0]	Sensor is performing outside of expected range	1.) Make sure the sensor is submerged in solution. 2.) Recalibrate sensor in a fresh batch of calibration standard. 3.) Reset sensor back to factory defaults and check reading in a calibration standard. Recalibrate. 4.) Call (800-446-7488) or contact In-Situ Technical Support (support@in-situ.com).
DIS[0]	Sensor is not set up correctly, being used outside of temperature or sensor range or returning a sentinel value due to internal malfunction or damage	1.) Verify that the RDO sensor cap is installed, the sensing foil is intact and the cap has not expired. 2.)Clean the surface of the sensor to remove any excess debris 3.) Verify that the instrument and sensors are not being used outside of temperature or sensor specifications. 4.) Verify that the sensor is not physically damaged 5.) Call (800-446-7488) or contact In-Situ Technical Support (support@in-situ.com).

Navigating VuSitu

Program your Aqua TROLL® 600 with the VuSitu mobile app for Android or iOS. Or use Win-Situ 5 software for a desktop PC.

VuSitu Mobile App

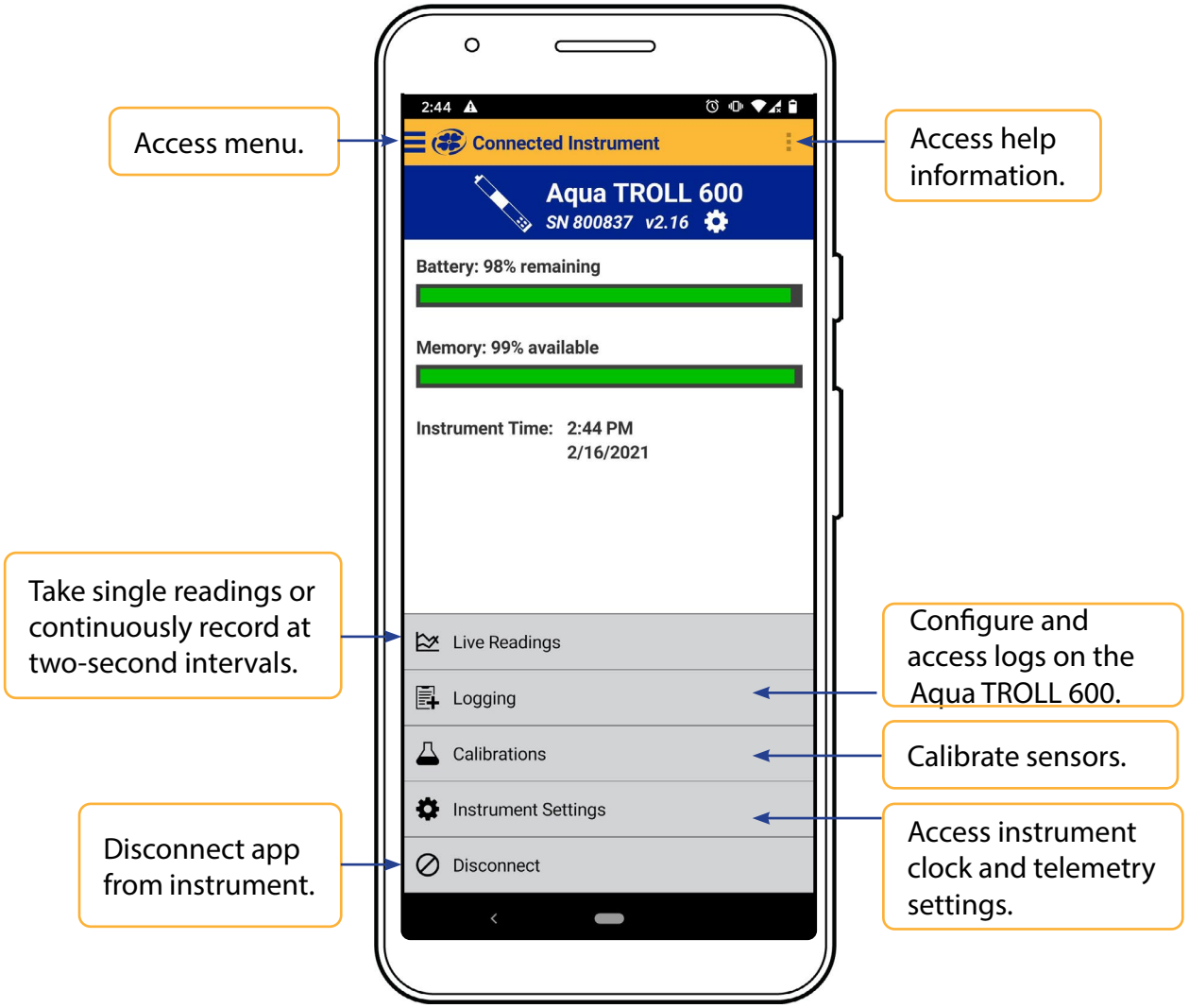
To avoid potential compatibility issues, it is important to use the most recent version of the VuSitu Mobile App. Install the latest version from the Google Play Store or Apple App Store.

Connecting with Bluetooth

The Aqua TROLL 600 can connect to a Bluetooth-enabled device for wireless communication with the VuSitu mobile app.

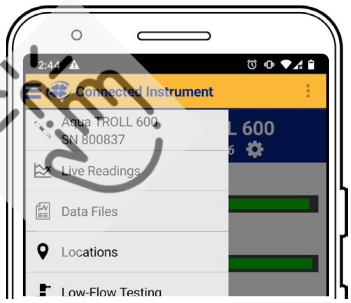
- If the Aqua TROLL 600 is connected to a Wireless TROLL Com, press the button on the Wireless TROLL Com. Then open VuSitu to connect.
- To connect to the Aqua TROLL 600 directly, turn on the Aqua TROLL 600 LCD screen by holding the sonde vertical with the sensor end facing up. Then open VuSitu to connect.

Connected Instrument Screen

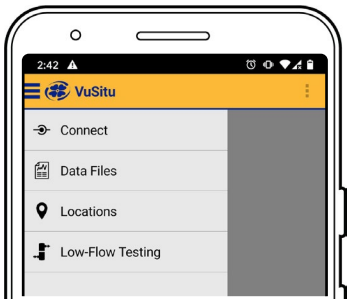


VuSitu Menu Options

The features available in the VuSitu mobile app vary slightly depending on the instrument to which it is connected.



Tap the menu icon in the upper left portion of the screen to view options. Tap the icon again to close.

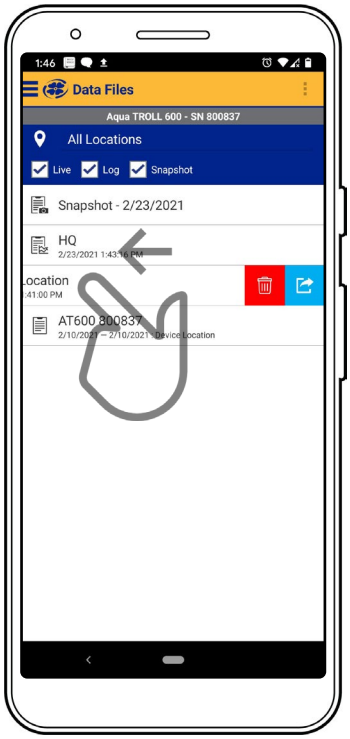


Some features aren't available when VuSitu isn't connected to an instrument.

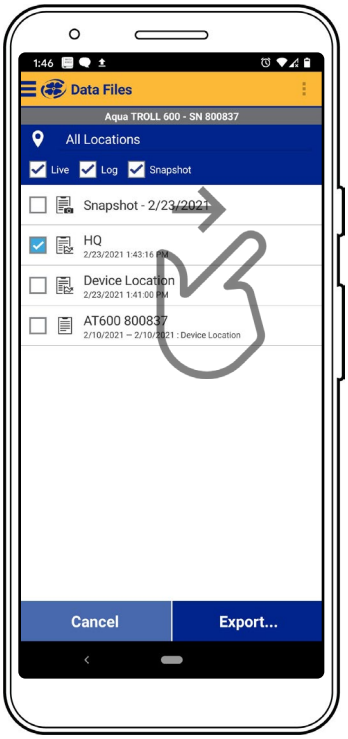
Selecting with Long-press and Swipe



Press and hold any item in a list of files. You can now select multiple files.



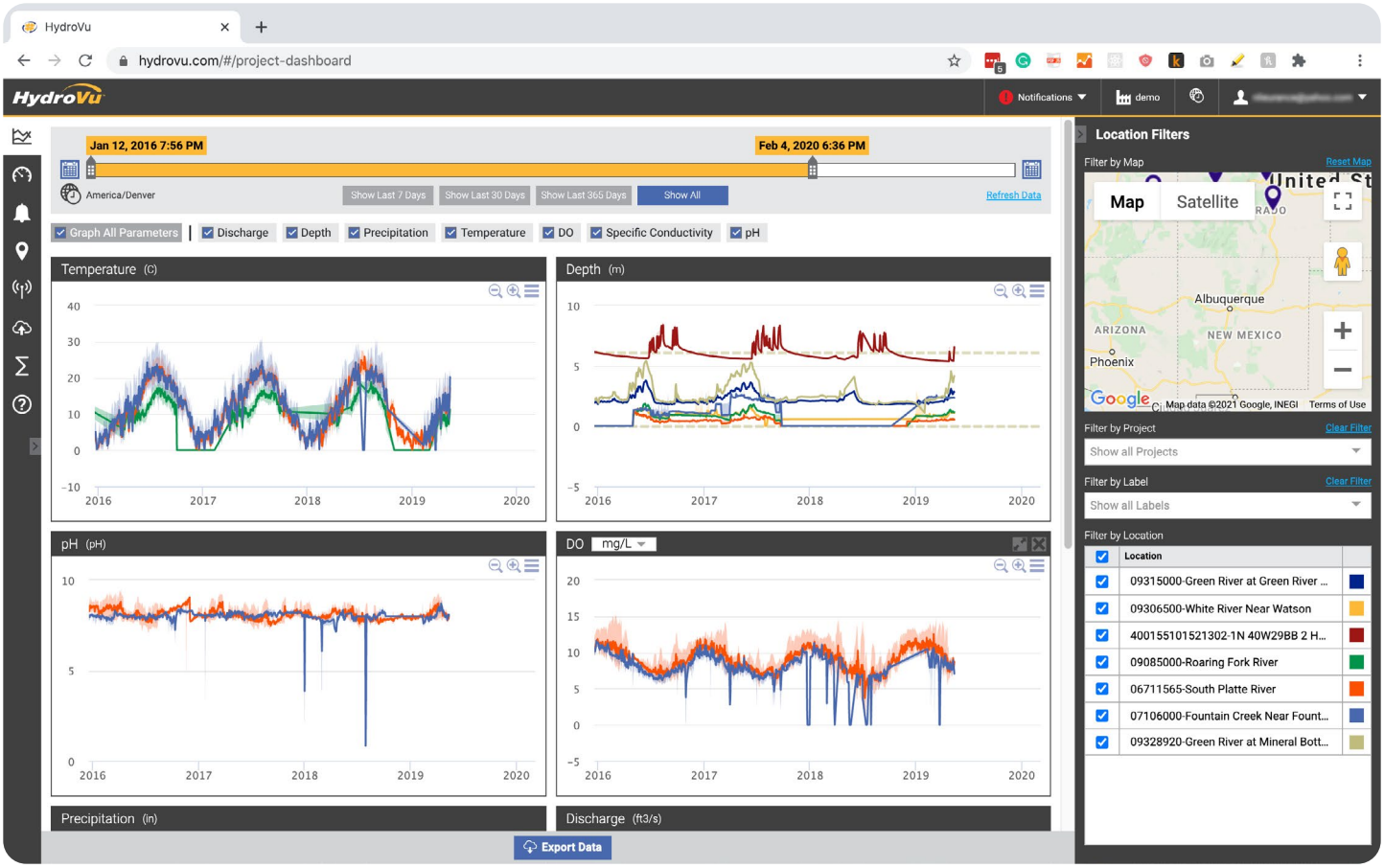
Press and swipe left to reveal the delete and share icons.



Press and swipe right to reveal the sharing icon.

HydroVu

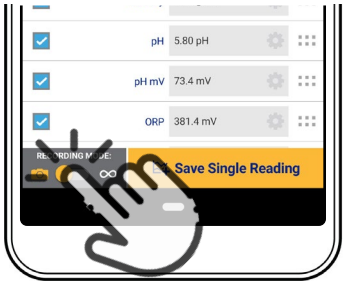
HydroVu is a data-management application that runs in the browser. Use it to manage data, view graphs, and configure telemetry devices for remote monitoring. See it at www.hydrovu.com.



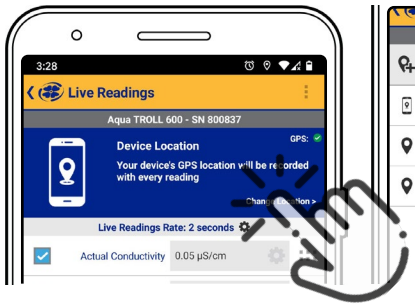
Live Readings in VuSitu

The live readings screen displays measurements taken from the instrument every two seconds. You can save these readings and share them via email or cloud storage.

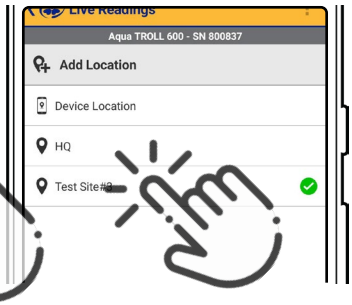
Snapshot Mode



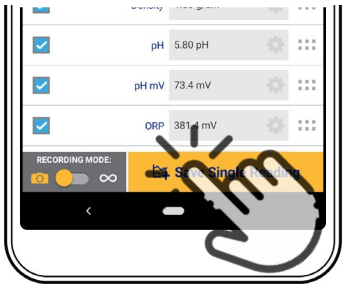
Tap the button on the bottom left to toggle between snapshot and live readings modes.



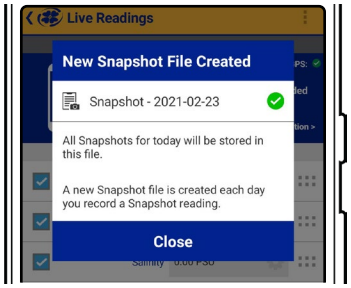
Tap **Change Location** in the top right corner if you wish to associate this data with a different location.



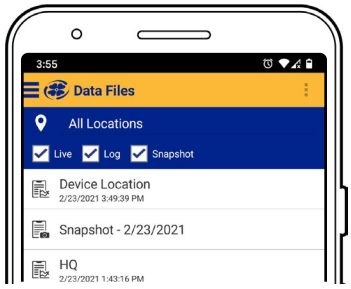
Choose the desired location and press **Save** in the bottom right corner of the screen.



Tap **Save Single Reading** to create a snapshot.

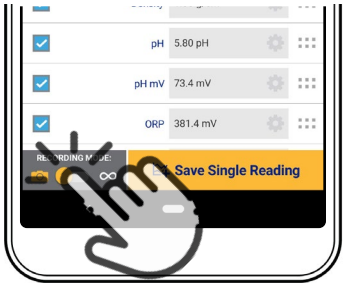


VuSitu confirms the new snapshot file.

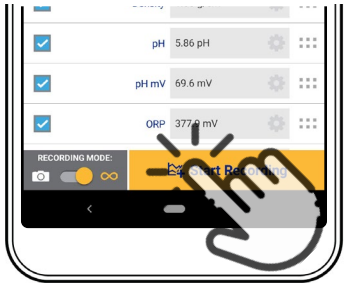


View the file from the Data Files screen.

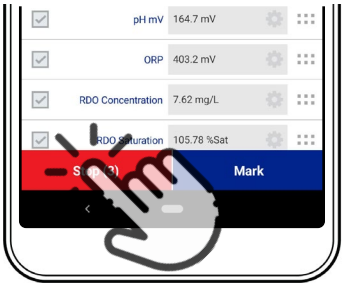
Live Readings Mode



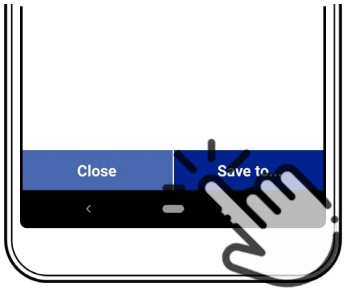
Tap the button on the bottom left to switch from snapshot mode to live readings mode.



Tap **Start Recording**. The instrument takes a reading every two seconds.



Tap **Stop** to end the recording. VuSitu displays a summary of the live readings data.

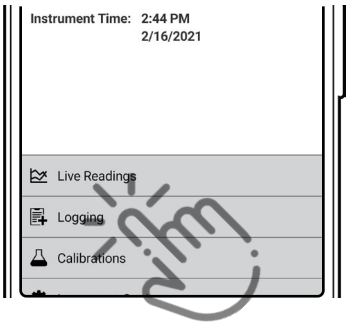


Tap **Save to** if you wish to share the Live Readings file via email or cloud storage.

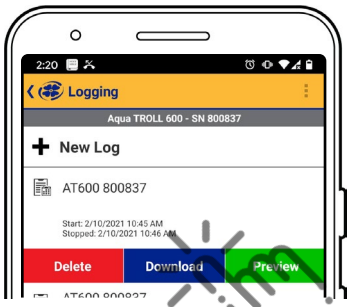
VuSitu Data

Downloading Your Data

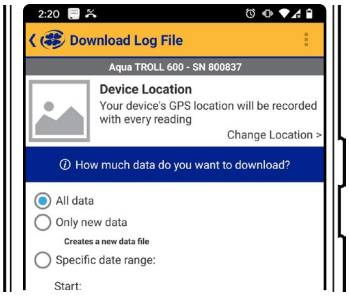
You can transfer a data file from your mobile device to a PC via Bluetooth, email it to yourself or any valid email address, or upload it to Google Drive.



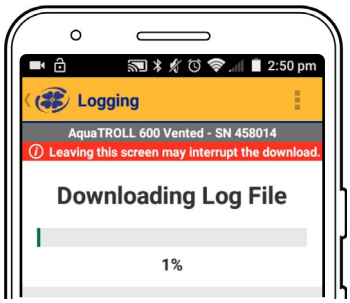
Pair VuSitu with the instrument. Select **Logging** from the Connected Instrument screen.



Tap a log and press the **Download** button.

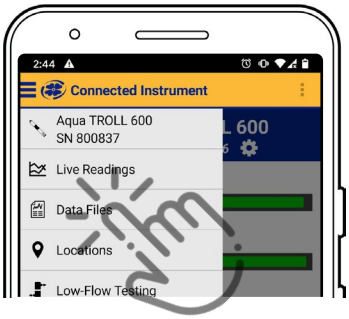


Choose the data you wish to download. To save the entire log to your phone, choose **All data**.

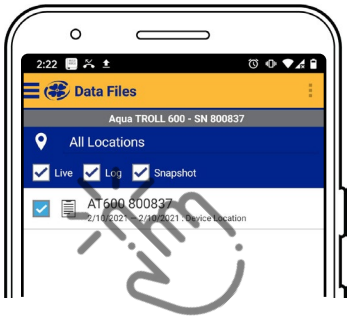


VuSitu displays a progress bar while downloading.

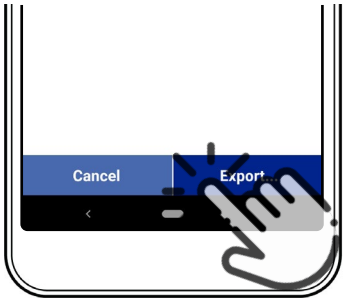
Sharing Data



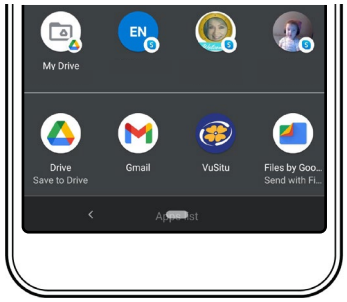
Select **Data Files** from the menu at the top left corner of the screen.



Tap and hold the name of the log you want to share.



Select **Export**.



Choose email, cloud storage, or another sharing option.

To save data locally on your mobile device, export to a third-party file management app.

Viewing Data on a Mac or PC

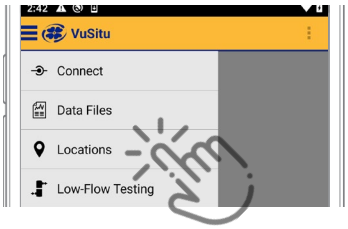
You'll need to extract your files to view them. To do that on a Mac, double-click the Zip folder. On a PC, right-click on the folder and choose **Extract**. Then open your files in Excel.

VuSitu Locations

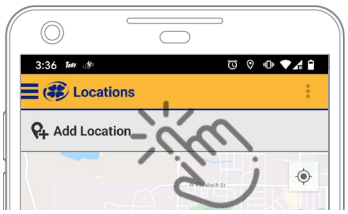
About VuSitu Locations

A VuSitu location represents the physical spot where an instrument collects data. You can create a VuSitu location for any monitoring site. If you don't create a location, your data defaults to "Device Location." Location names appear on the live readings screen, in snapshot files, and in log files.

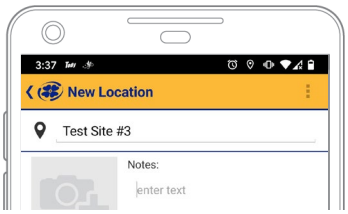
How to Create a Location



Select **Locations** from the main menu.



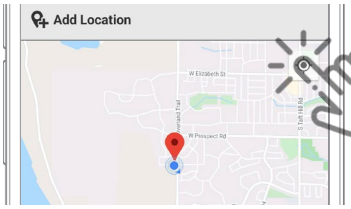
Tap **Add Location**.



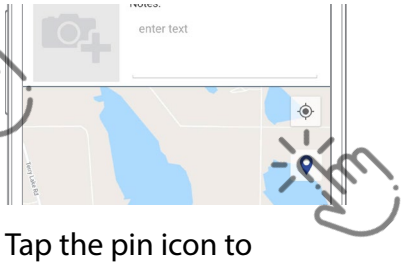
Enter a name for the location. You can also add notes.



If desired, tap the camera icon to take a photo of the new location.



To home in on your mobile device's current location, tap the button on the top right.

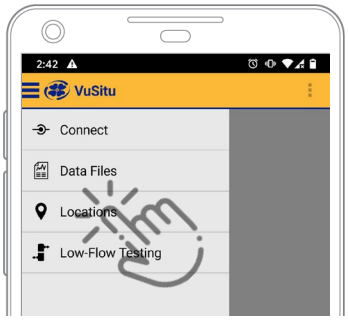


Tap the pin icon to establish the location on the map.

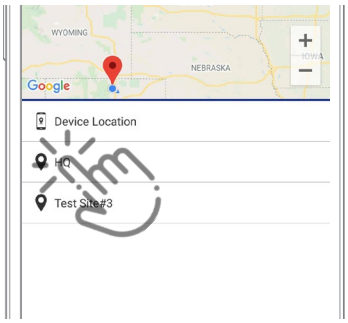
As an alternative, you can manually enter latitude and longitude values and tap **Apply**. Or, tap and hold a specific point on the map to drop a pin there.

How to Select a Location

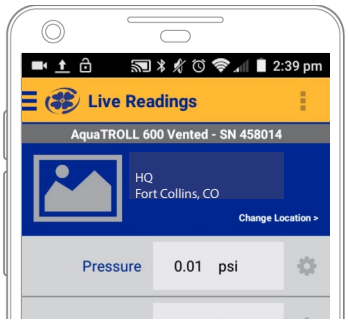
Data is associated with the Location that is displayed on the Live readings screen. After you have created a Location, you must select it in order for your data to be associated with the Location.



Select **Locations** from the app menu.

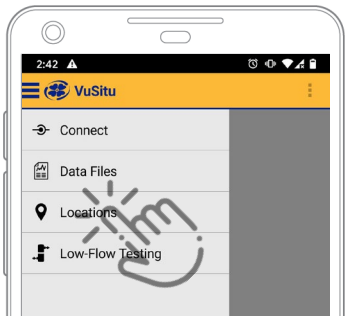


Tap a location to select it.



New live readings data will be associated with this location until you select another.

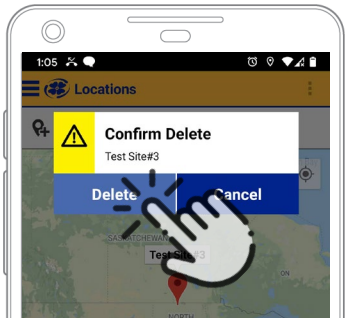
How to Edit or Delete a Location



Select **Locations** from the app menu.



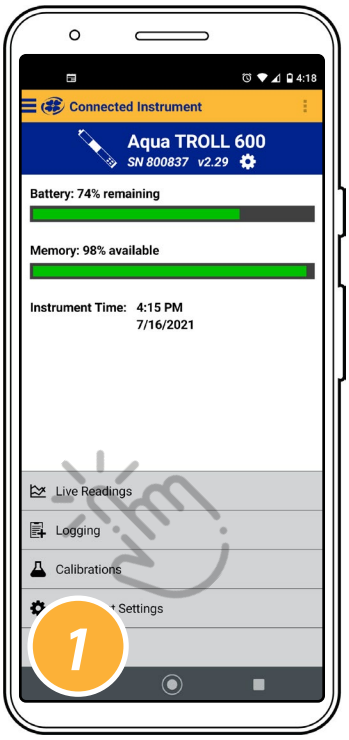
Tap the location you wish to delete and swipe left. Tap the trash icon.



Confirm by tapping **Delete**.

How to Create a Log with VuSitu...

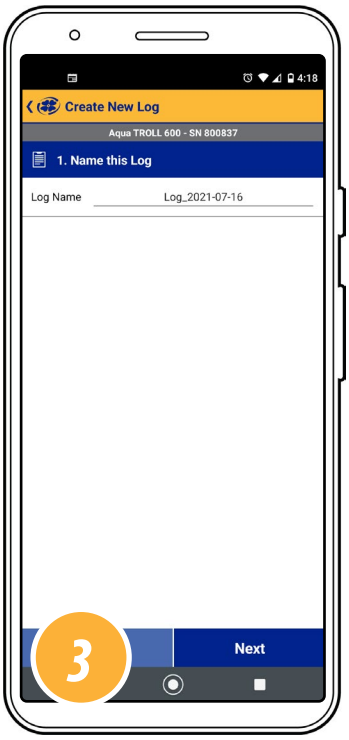
Connect to the instrument via VuSitu to create a log. Then follow the on-screen instructions. You can choose a start time for the log or start the log with a button press.



Select **Logging**.



Tap **New Log**.



Follow the on-screen instructions to create and schedule a log.

Remote-Monitoring Configuration (Telemetry)

VuLink can provide power to the Aqua TROLL 600 and uploads data to the HydroVu Data server.

1 Remove the battery pull-tab.

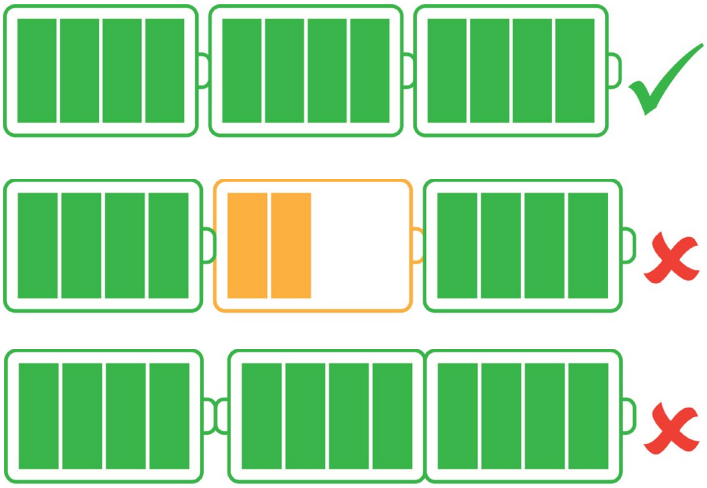


Remove the battery cover by twisting it counter-clockwise and pulling down.



Remove the yellow pull tab to allow current to flow through the batteries.

Never mix old and new batteries, or Lithium and alkaline batteries. Make sure all three batteries are installed in the same orientation.



2 Connect the instrument.



Align the flat edge of the connector with the flat edge inside the cable.



Twist the cable until it clicks into the secure postion.



Connect the cable to your instrument.

3 Press the button on the VuLink control panel.

Connecting to a cellular network can take up to 10 minutes in the following situations:

- The first time VuLink powers up
- When VuLink hasn't been powered up in several weeks or months



Pressing the button starts the instrument connection process.



All LEDs turn green for one second. The battery status LED changes according to power level.



Next, the connection status LED and Bluetooth status LED blink.



The connection status LED turns solid green, indicating VuLink is connected to an instrument.



Once linked to an instrument, VuLink attempts to connect to a data network.



When the modem status LED turns green, VuLink begins connecting to HydroVu. The data LED blinks.



All LEDs except the Bluetooth status indicator turn green.

By default, VuLink reads all available parameters every hour and transmits to the cloud once daily. You can also connect to the VuLink using the VuSitu Mobile App to configure a custom log. See the VuLink manual for more infomation.

Connecting to Win-Situ on a PC

Connecting to Win-Situ via USB

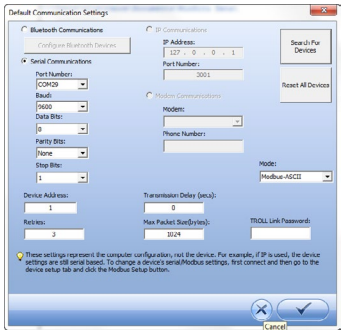
Download and install Win-Situ by visiting www.in-situ.com. The Wireless TROLL Com must be connected to the sonde and powered on to connect the instrument to Win-Situ.

You can connect a Wireless TROLL Com to a PC with the included USB cable. Plug the cable into the port at the top of the TROLL Com and the USB port on your PC.





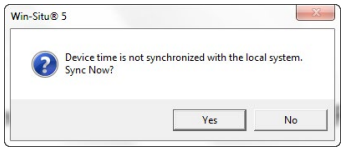
Open Win-Situ. Select **No** when asked to connect now.



Click Preferences > Com Settings from menu bar and choose correct com port. Select Serial Communications button. Click check mark button.



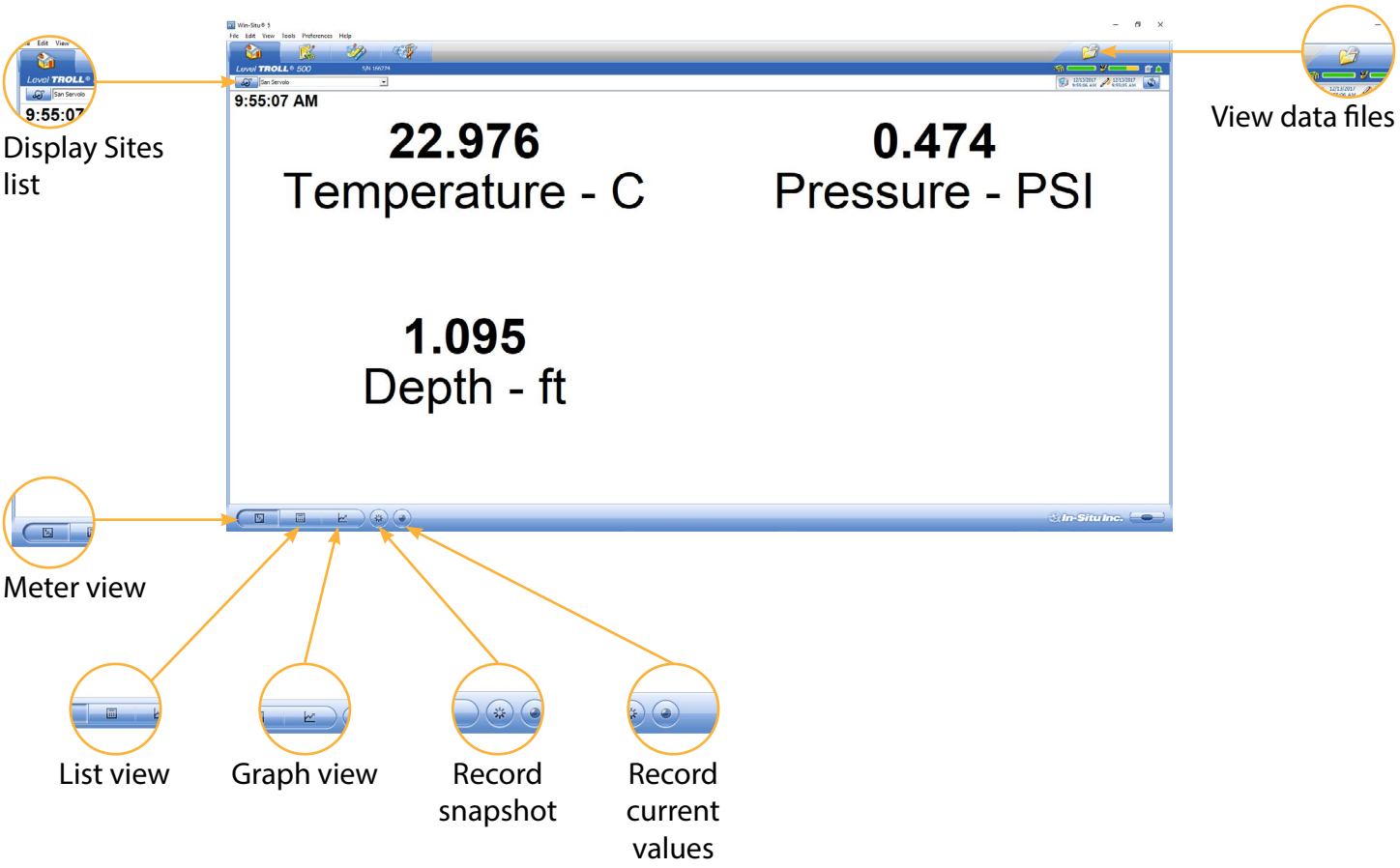
Click the yellow connect button at the bottom right of the screen.



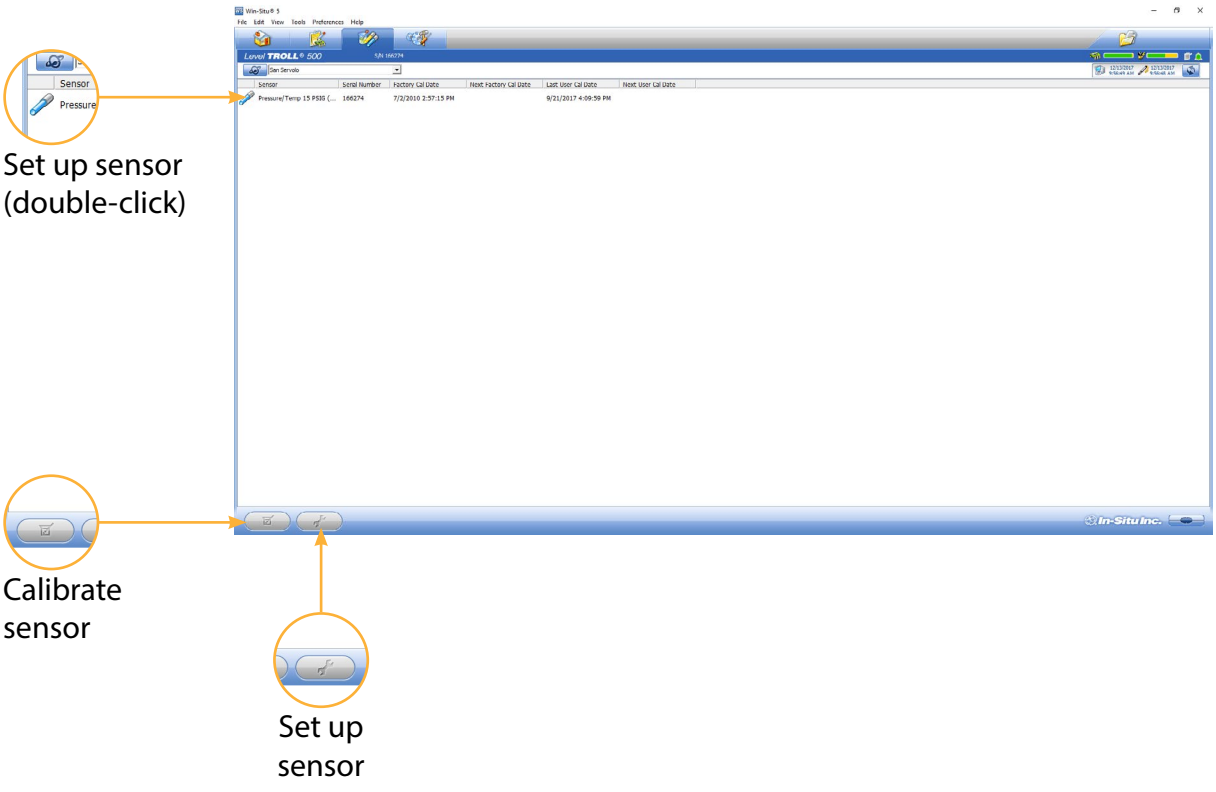
Click Yes if prompted to sync device time with local system.

Navigating the Win-Situ Interface

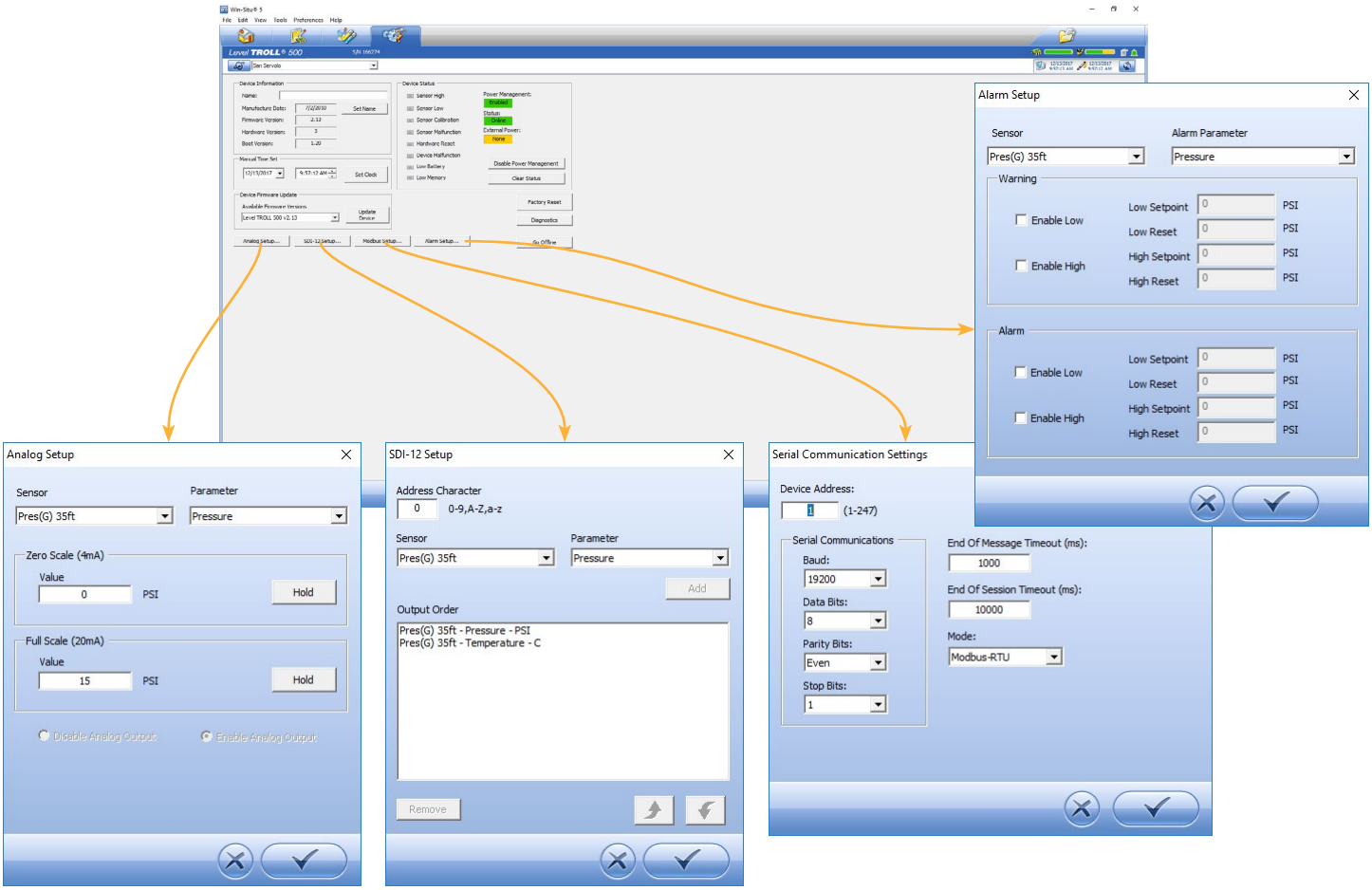
Home Tab



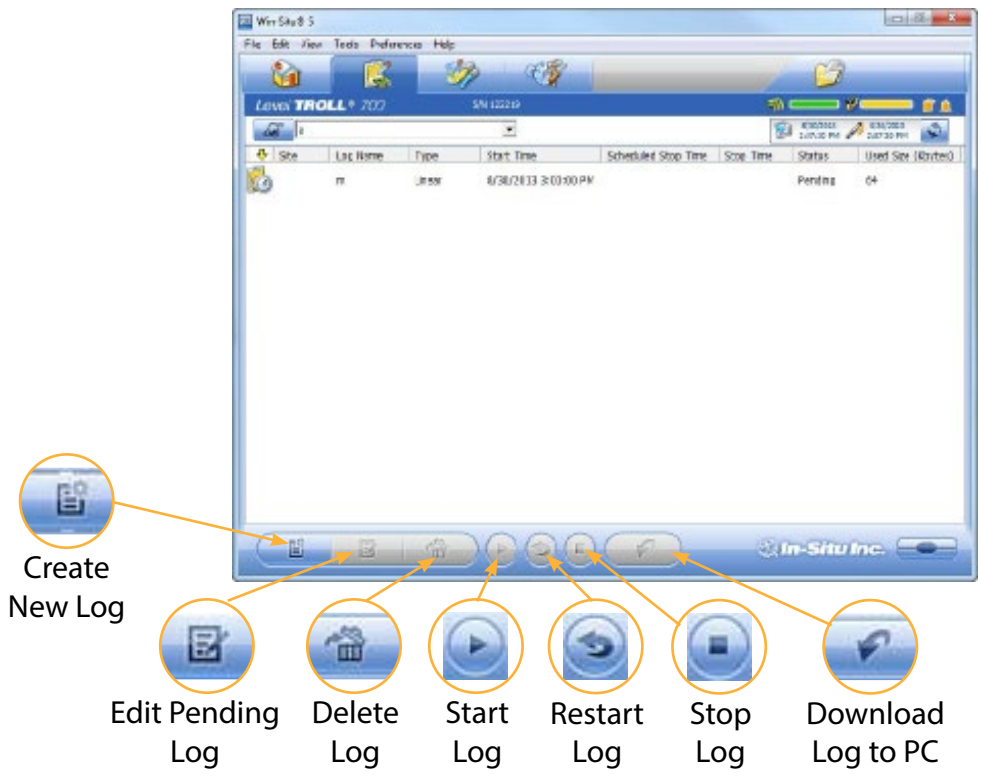
Sensor Tab



Device Setup Tab



Logging Tab



Log Status Indicators

	Ready
	Pending
	Running
	Suspended
	Stopped
	Deleted
	Invalid

BaroMerge

Using BaroMerge Software

BaroMerge Software is used to post-correct absolute (non-vented) level sensor data to eliminate barometric pressure effects from the measurements. BaroMerge Software can be accessed through the Win-Situ 5 Software Tools menu. BaroMerge provides three options to correct data.

- Fixed Correction—A single offset value is applied to all selected log data. Use this option if you know the barometric pressure of the site during the log, and know that it did not change.
- Manual Entry—Specify two or more correction values to apply to the log data. Use this option if you wish to manually enter a data set of barometric pressure values.
- BaroTROLL log file—Absolute level sensor data points are individually corrected to reflect barometric pressure changes that were logged by a BaroTROLL instrument during the approximate time period.



Baro Merge Input—Manual Entry

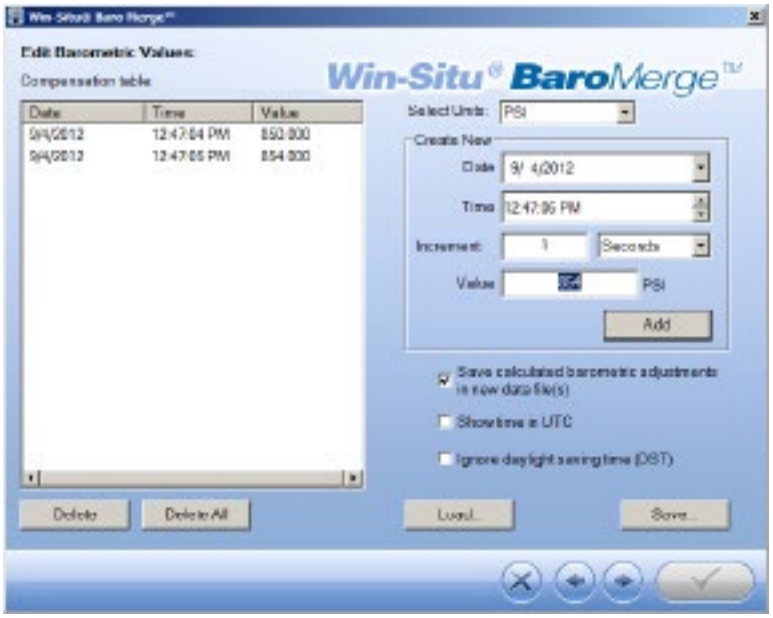
When you select the Fixed Correction and Manual Entry options, it is important to know the barometric pressure for the general time period covered by the log or logs you want to correct.

1 From the Tools menu, select Win-Situ BaroMerge.



1 Select the Enter one or more values manually option.

2 The compensation table appears that allows you to build a table of barometric data that corresponds to the time the log was recorded. The compensation table has three preference options:



- The first option, Save calculated barometric adjustments in the new data file(s) is the default option. It adds additional columns depending on which parameters were selected for the absolute/non-vented log in the corrected BaroMerge file that uses the compensation table values. This is intended to show how the adjustments were done in the BaroMerge file. If you do not want to show these adjustments, clear this option.
- When the second option, Show time in UTC is selected, the compensation table time stamp displays in Coordinated Universal Time (UTC) time, formally known as Greenwich Mean Time (GMT).
- If the third option, Ignore daylight saving time (DST) is selected, the compensation table time stamp format without the daylight savings time adjustment will be shown.

3 Build a table that contains at least two barometric pressure values.

4 Click the right arrow and select the absolute (non-vented) log file or files you intend to correct.

5 Click the check mark and the barometric compensation is applied.

6 Compensated data files can be viewed or exported from the Data tab.

Baro Merge Input—Fixed Correction

If you select the Apply a fixed correction option, a single correction is applied to all values in the log. To use this correction method you need barometric pressure values from a reliable source. Choose a single value that represents the actual ambient barometric pressure during the time period the log was recorded. You also need to know the file names of the logs you want to correct.

1 From the Tools menu, select Win-Situ Baro Merge.



2 Select the Apply a fixed correction option.

3 Enter the barometric correction value and select units from the drop-down menu.

4 Click the right arrow button.

5 Select the log files to which the correction will be applied and click the check mark button.

6 Compensated data files can be viewed or exported from the Data tab.

BaroMerge Input—BaroTROLL File

Log files that contain absolute data can be barometrically compensated using values logged by the In-Situ Inc. BaroTROLL Instrument. Select this method when you have access to a BaroTROLL log file covering approximately the same time period as the data file you intend to correct.
To use this correction method, you need the name of the BaroTROLL log file and the name(s) of the absolute log file(s) you want to correct.

1 From the Tools menu in Win-Situ 5 Software, select Win-Situ BaroMerge.



2 Select the "Use a BaroTROLL file:" option.

3 Click the browse button to the right of the file field.

4 Select a BaroTROLL file and click the check mark.

5 Values from the BaroTROLL file will be displayed in the next window. You can edit these values if necessary.

6 Click the right arrow button.

7 Select the log file(s) you intend to correct and click the check mark.

8 Compensated data files can be viewed or exported from the Data tab.

BaroMerge Output

Your original log file is not changed. A new, corrected log file with the same name and path is created. The original ".wsl" extension is replaced by "-Baro Merge.wsl".

Post Level Correction within Baro Merge

It is also possible to post correct a level reference in data collected from an absolute sensor if the data has been compensated through Baro Merge Software.

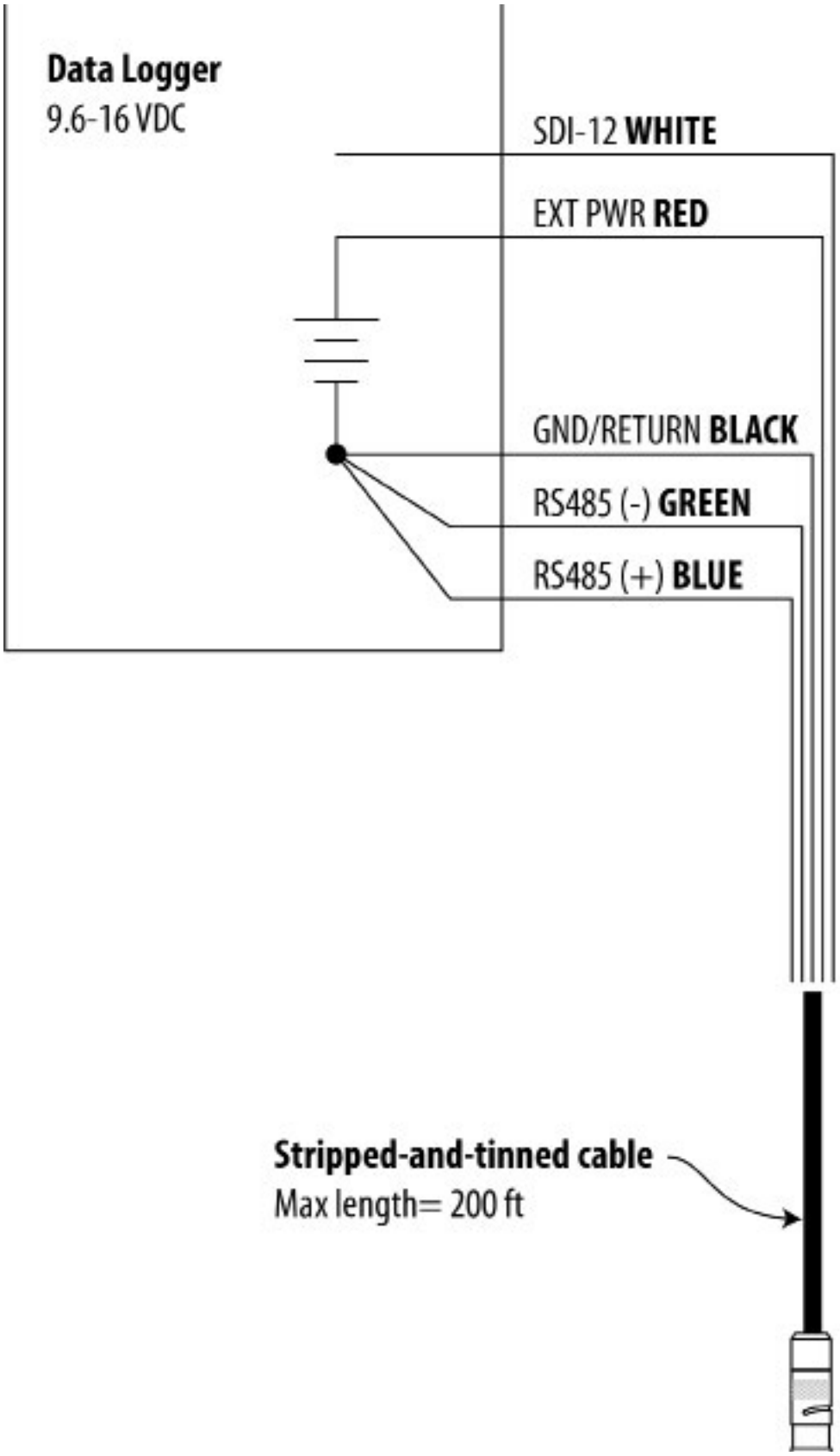
1 Follow the steps to compensate the absolute data for barometric pressure.

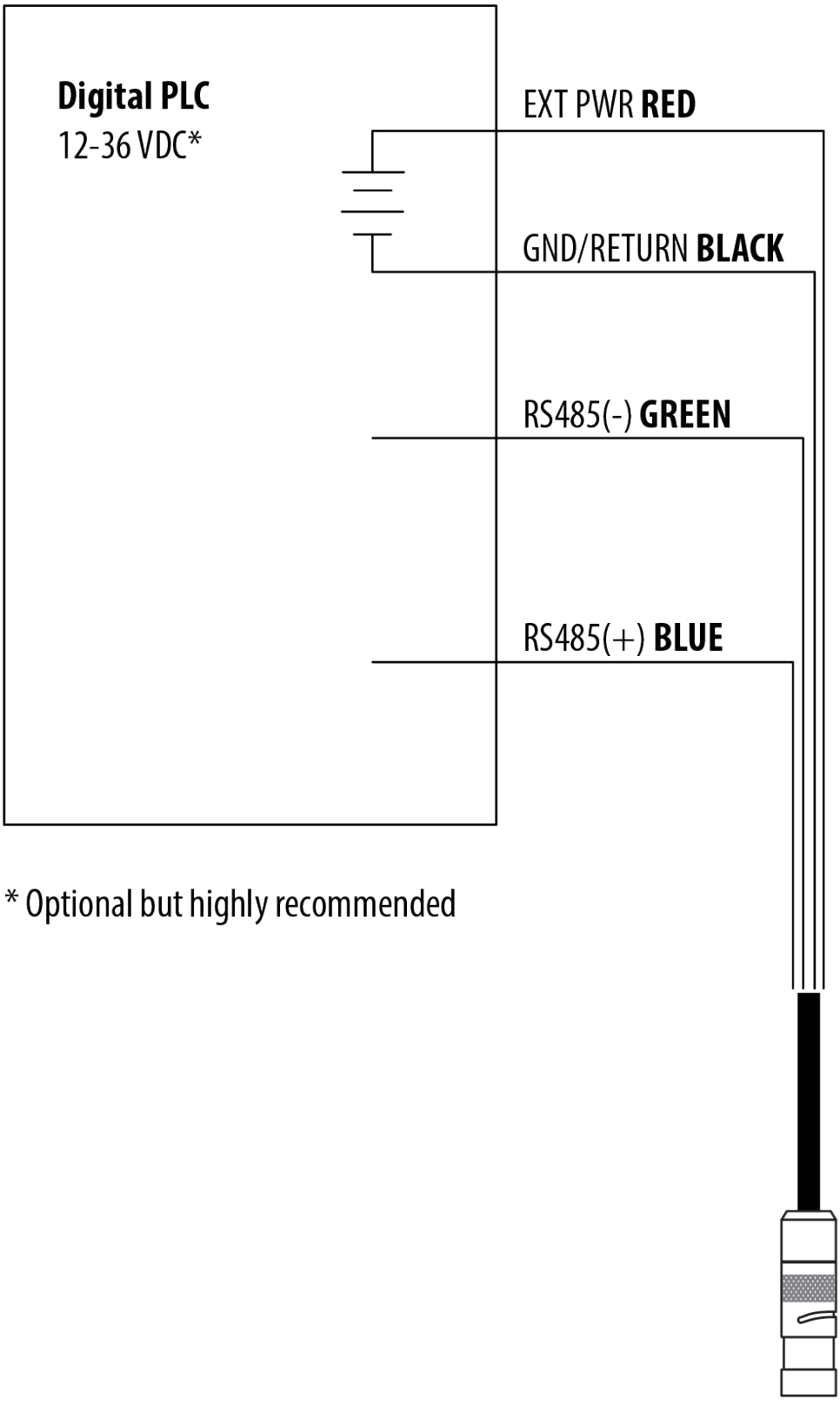
2 When you reach this screen in the Wizard, you can select the check box to Post correct files for level.



Connecting the Aqua TROLL 600 to a PLC or Data Logger

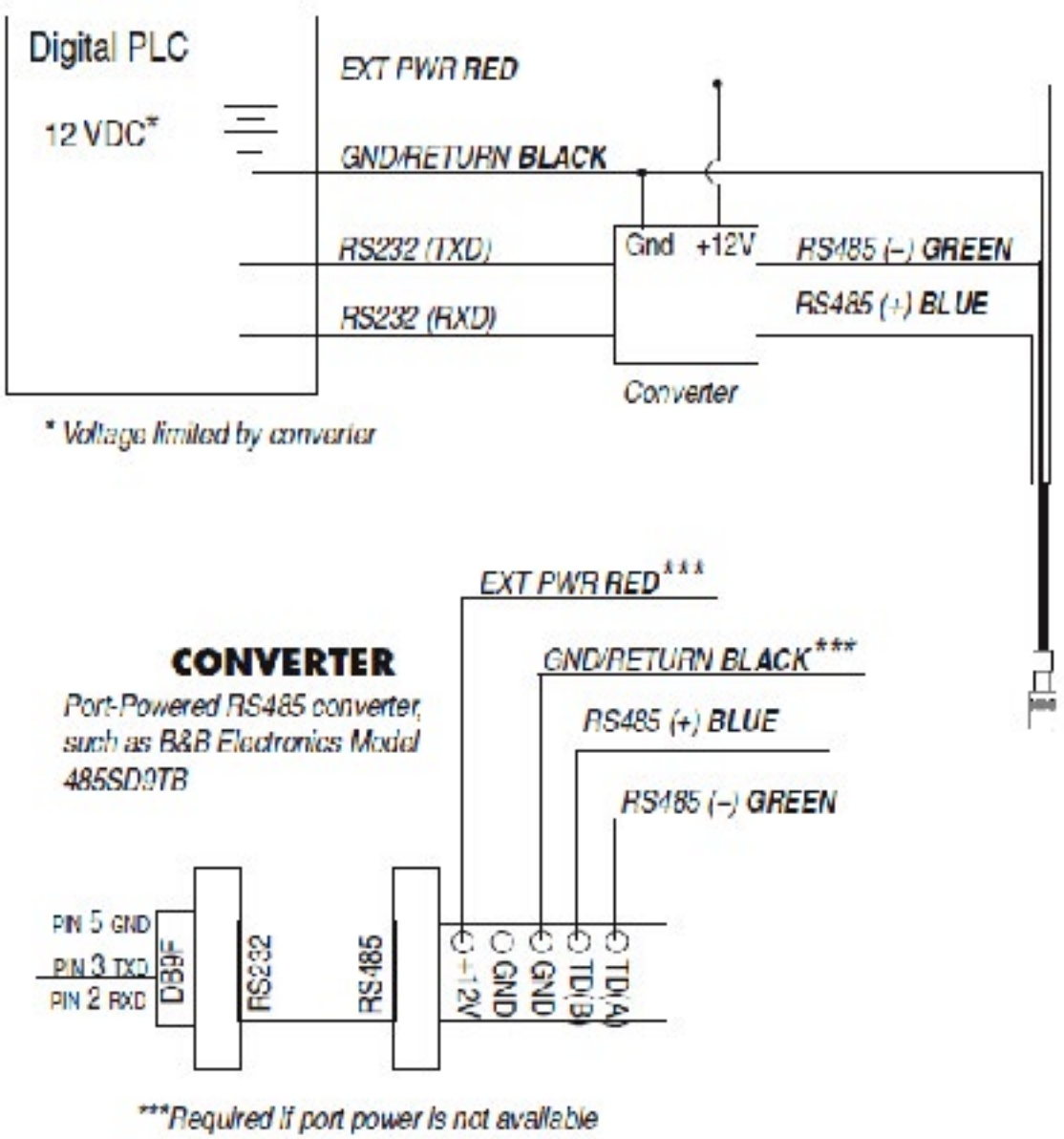
SDI-12 3 Wire





* Optional but highly recommended

Modbus Master with RS232 (Converter Required)



Modbus PLC Interface

Overview

The Modbus PLC Interface is a simplified method of communicating with the Aqua TROLL 600 using the Modbus protocol. It reduces programming complexity and allows the user to remove sensors and reinstall them in different ports. Please observe the following limitations when using this interface:

- Only one sensor of any sensor model can be used in the sonde (for example: only one turbidity sensor can be installed).
- If a parameter is provided by more than one of the installed sensors, the interface will return the first value available.
- Firmware version 1.71 or later must be installed on the sonde.

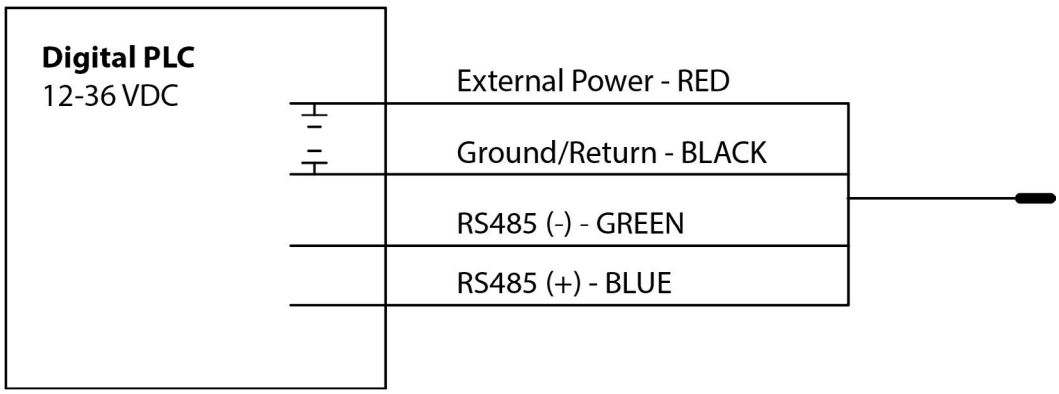
For information about the full Modbus capabilities of your sonde, see the Aqua TROLL 500/600 Interface Specification at www.in-situ.com/support/type/documentation.

Setting Up Instrument

1. Install the sensors and turn on the display by holding the instrument vertically.
    a. Ensure the display turns on and check the LCD to ensure the sensors are working.
2. The setup below is using the instrument's factory default settings. Use WinSitu or VuSitu to reset the instrument to
factory defaults if they have been changed.
    a. Take note of any changes in default units setup.

Wiring the Modbus Master

Connect the Twist-Lock termination to the instrument and wire the stripped-and-tinned connection as shown below:



Programming the PLC

1. Setup the serial communication the following values:

Mode	Start Bit	Baud Rate	Data Bits	Parity	Stop Bit
RTU	1	19200	8	Even	1

2. Set the device address to: 1
3. Set the PLC to wake-up the device by sending any Modbus command.
    a. This could be a carriage return, reading the slave id or reading any register.
4. Read the discovery register using Appendix A to trigger the instrument to scan the sensors.
    a. The return value can be discarded.
    b. Each register is a holding register. Some PLCs require you to add 40000 to the register number or address. For example: 9301 would be 49301.
    c. Alternatively, you can prompt the instrument to discover its sensor mapping by connecting it to the VuSitu mobile app or Win-Situ software.
5. Select the register to read on the PLC using Appendix B
    a. Some PLC devices use the register number directly in programming statements, others use register
    addresses, which are one less than the register number; the programmer must adhere to the PLC's programming style
    b. Each register is a holding register. Some PLCs require you to add 40000 to the register number or address. For example: 5451 would be 45451.
6. Set the type of register to: 32-bit float
    a. If asked by the PLC this is 2 registers
7. Set the byte order to: Big Endean (MSB)
    a. This should be the default and may not be configurable on all PLCs

Reading Parameters

To determine the starting register number for a given parameter register block, first determine its parameter id by looking in the sensor's parameter tables. Then calculate the starting register number of the parameter block using the following equation.

Starting Register = (Parameter Id – 1) x 7 + 5451

For example, for the Conductivity Sensor, the parameter id for specific conductivity is 10 (bit 9 will be set in register 6984 if it is available). The starting register number for the specific conductivity register block is thus (10 – 1) x 7 + 5451 = 5514.

The starting register for each parameter points to a block of 7 registers that contain the following information.

Register Offset	Size (Registers)	Mode & Access Level (R/W)	Data Type	Description
0	2	R	float	The measured value from sensor
2	1	R	ushort	Data Quality Id: If this is 0 then there are no errors or warnings. See: Full System Specification
3	1	R/W	float	Units Id for the measured value. The default values are listed in the table below.
4	1	R	ushort	Parameter Id: The ID of the parameter for this location. See: Full System Specification
5	2	R/W	float	Off line sentinel value: The value that's returned on error or if the parameter isn't available. The default sentinel is 0.0

Care and Maintenance

Maintenance Schedule

For best results, send the instrument to the manufacturer for factory calibration every 12 to 18 months.

User-Serviceable Parts



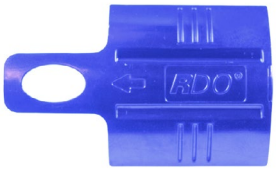
O-rings

Lubricate O-rings during initial setup. Check and replace O-rings if worn, damaged, or discolored.



Sensors

See the sensor instruction sheets for details about maintaining and replacing.



RDO Sensor Cap

Refer to the sensor cap instruction sheet for details.

Storage

Short-term (less than one week)



Remove the restrictor and the end cap.



Put the restrictor on the instrument in calibration mode.



Pour 15 mL (5 oz) of clean water into the restrictor and replace the cap.



Thread the restrictor onto the sonde and store.

Long-term (more than one week)



Remove the sensors and wiper.



Dampen the sponge inside the pH sensor storage cap with Storage Solution or pH 4 calibration standard.



Replace the caps at both ends of the sensor. Use electrical tape to seal the storage cap.



Thread the restrictor onto the sonde.

Store the sonde and sensors at temperatures between -5° and 65° C.

Cleaning the Sonde

Rinse the sonde thoroughly, clean with warm water and mild soap, then rinse the sonde again. Allow to air dry.

Prevent water from entering the cable connector.

Cleaning and Storing the pH/ORP Sensor

Routine Maintenance

If the ORP platinum electrode is dull or dirty, it can be cleaned with a swab and methanol or isopropyl alcohol. Rub the electrode gently until it is shiny.
The pH sensor must be kept moist for the life of the sensor.
The sensor fill solution has a shelf life of 2 years. Replace the fill solution every 5 to 6 months or when:

1 The sensor fails to calibrate within the acceptable slope and offset range.
2 Sensor readings vary.
3 Readings during calibration at pH 7 are greater than +30 mV or less than -30 mV.
4 Sensor is slow to respond.

If the sensor fails to calibrate after you replace the fill solution, replace the reference junction.

Replacing the Filling Solution



Remove sensor from sonde and unscrew reference junction.



Discard old solution.



Insert tube from filling solution bottle into sensor.



Squeeze solution into reservoir until full. Slowly remove tube.



Reinstall reference junction and wipe sensor body dry.



Soak sensor in tap water for at least 15 minutes.

If necessary, thoroughly clean the sensor connector to remove filling solution: Using a disposable pipette, fill the connector with isopropyl alcohol (70% to 100%), Shake to dry. Repeat 3 times. Dry overnight. When thoroughly dry, calibrate the sensor.

Replacing the Junction

Replace the junction when the sensor fails to calibrate with a reasonable slope and offset, even after you have replaced the filling solution.

1 Unscrew the reference junction and discard.

2 Replace the filling solution and screw in a new reference solution.

3 Soak for 15 minutes, then calibrate the sensor.

Keep the junction damp at all times to avoid a lengthy re-wetting process.

Cleaning

Begin with the gentlest cleaning method and continue to the others only if necessary. Do not directly wipe the glass bulb. To clean the pH sensor, gently rinse with cold water. If further cleaning is required, consider the nature of the debris.
To remove crystalline deposits:

1 Clean the sensor with warm water and mild soap.

2 Soak the sensor in 5% HCl solution for 10 to 30 minutes.

3 If deposits persist, alternate soaking in 5% HCl and 5% NaOH solutions.

To remove oily or greasy residue:

1 Clean the sensor with warm water and mild soap.

2 Methanol or isopropyl alcohol may be used for short soaking periods, up to 1 hour.

3 Do not soak the sensor in strong solvents, such as chlorinated solvents, ethers, or ketones, such as acetone.

To remove protein-like material, or slimy film:

1 Clean the sensor with warm water and mild soap.

2 Soak the sensor in 0.1 M HCl solution for 10 minutes and then rinse with deionized water.

After cleaning, rinse the sensor with water, and then soak overnight in pH 4 buffer.

Storage



Dampen the sponge inside the pH sensor storage cap with Storage Solution or pH 4 calibration standard.



Replace the caps at both ends of the sensor. Use electrical tape to seal the storage cap.

Do not store the pH sensor in DI water because it will deplete the reference solution and drastically reduce the life of the sensor.

Cleaning and Storing the RDO Sensor

Routine Maintenance

1 Leave the sensor cap on.

2 Rinse the sensor with clean water.

3 Gently wipe with a soft cloth or brush if biofouling is present.

4 If extensive fouling or mineral buildup is present, soak the sensor in vinegar for 15 minutes, then soak in deionized water for 15 minutes.

Do not use organic solvents—they will damage the sensor cap. Do not remove the sensor cap when rinsing or brushing.

5 After cleaning the sensor, perform a 2-point calibration.

Cleaning the Optical Window

Clean the optical window only when changing the sensor cap.

1 Remove the cap.

2 Gently wipe the sensing window with the supplied lens cloth.

Do not wet the lens with any liquid.

Storage

Prior to installation, store the sensor body and cap in the factory supplied containers.
Once installed on the sonde, the RDO sensor can be stored wet or dry depending on the sensor configuration of the sonde.

Never store the RDO sensor without the sensor cap once it has been installed on the sonde.

Cleaning and Storing the Conductivity Sensor



Soaking the sensor in vinegar for longer than one hour can cause serious damage.

Begin with the most gentle cleaning method and continue to the other methods only if necessary.
To clean the conductivity sensor face, gently rinse with clean, cold water. If further cleaning is required, consider the nature of the debris.
To remove crystalline deposits:

1 Clean the sensor face with warm water and mild soap.

2 Use a soft brush to gently clean the sensor pins and temperature button. Ensure removal of all debris around the base of the pins and button.

3 If crystalline deposits persist, soak in 5% HCl for 10 to 30 minutes followed by warm soapy water and soft brushing.

4 If deposits persist, alternate soaking in 5% HCl and 5% NaOH solutions followed by warm soapy water and soft brushing.

To remove oily or greasy residue:

- Clean the sensor face with warm water and mild soap.
- Using a soft brush, gently clean the sensor pins and temperature button. Ensure removal of all residue around the base of the pins and temperature button.
- Isopropyl alcohol may be used for short soaking periods, up to one hour.
- Do not soak in strong solvents such as chlorinated solvents, ethers or ketones (such as acetone).

To remove protein-like material, or slimy film:

- Clean the sensor face with warm water and mild soap.
- Using a soft brush, gently clean the sensor pins and temperature button. Ensure removal of all material/film around the base of the pins and temperature button.
- Soak the sensor in 0.10% HCl for 10 minutes and then rinse thoroughly with distilled water.

Storage

Prior to installation, store the sensor in the factory supplied container.
Once installed on the sonde, the Temperature Sensor and Conductivity Sensor can be stored wet or dry depending on the sensor configuration of the sonde. For the best accuracy over instrument life, keep the conductivity cell submersed in water for 24-48 hours prior to calibration and deployment.

Cleaning and Storing the Turbidity Sensor

Routine Maintenance

The optical windows should be clear of foreign material. To clear material gently rub the sensing windows using clean water and a soft cloth or swab. Do not use solvents on the sensor.

Storage

Prior to installation, store the sensor in the factory supplied container. Once installed on the sonde, the turbidity sensor can be stored wet or dry depending on the sensor configuration of the sonde.

Replacing Wiper Bristles

Wiper bristles need to be replaced based on site conditions. In-Situ recommends replacing bristles at least every 12 months or when visibly bent, damaged, or fouled.



Replace the Bristles

1 Slide both bristle sets out of the wiper head.

2 Insert new small bristle set into the small slot and the large bristle set in the large slot.

Replace the Entire Brush

1 Loosen the set screw near the base of the wiper head.

2 Slide the wiper head off the wiper shaft.

3 Slide the wipe head on to the wiper shaft, and position the wiper head so the set screw faces the flat part of the wiper shaft.



4 Tighten the set screw near the base of the wiper head.

Cleaning the Copper Antifouling Restrictor

When copper is deployed in environmental waters, particularly marine environments, the copper will oxidize and its biocidal properties decrease. Cleaning the copper restores the effectiveness of the restrictor's antifouling capability.

1 Remove the restrictor from the sonde.

2 Remove the restrictor end cap.

3 Submerge the restrictor in white vinegar (acetic acid) for 24 hours.

4 Rinse the restrictor in water and air dry.

More Information

To learn more about the Aqua TROLL 600, telemetry, software and other In-Situ products, see the resources listed below.

1 Visit www.in-situ.com

Find information about In-Situ water quality, water level, telemetry and other products. Download software, manuals and product instructions.

2 View the In-Situ YouTube channel.

Get video instructions for the Aqua TROLL 600 and other instruments. Watch quickstart videos and other tutorials.

3 Call In-Situ's technical support team.

For further instructions and help with technical questions, call the In-Situ support line at 1-970-498-100.

Declaration of Conformity

Manufacturer: In-Situ, Inc.
221 East Lincoln Avenue
Fort Collins, CO 80524
USA

Declares that the following product:

Product name: Aqua TROLL® 600 Multiparameter Sonde
Model: Aqua TROLL® 600
Product Description: Multiparameter water quality data logger

is in compliance with the following Directive

2004/108/EC for Electromagnetic Compatibility (EMC) Directive

and meets or exceeds the following international requirements and compliance standards:

- **Immunity**
  EN 61326, Electrical Equipment for Measurement, Control and Laboratory Use, Industrial Location

- **Emissions**
  Class A requirements of EN 61326, Electrical Equipment for Measurement, Control and Laboratory Use

Supplementary Information:
The device complies with the requirements of the EU Directives 2004/108/EC and 2006/95/EC, and the CE mark is affixed accordingly.

Ben Kimbell
VP of R&D
In-Situ, Inc.
August 25, 2015

RoHS CE FC

FCC (SSSBC127-X)

Appendix

Appendix A: Parameter Discovery

The first register read in a PLC measurement sequence should be a 14-register block beginning with register number 6984. A read of these registers triggers the sonde to scan its sensor ports and update its sensor map. This guarantees that the sonde has properly registered any changes to the sensor configuration a user may have made since the last measurement sequence. The bitwise contents of these registers indicate which parameter IDs (1 to 219) are currently available from the sonde according to the table below. Refer to Appendix B for a description of parameter IDs.

Parameter ID Map					
Register	**Bit**				
	15	**14**	**13...2**	**1**	**0**
6984	16	15	14...3	2	1
6985	32	31	30...19	18	17
6986	48	47	46...35	33	33
6987	64	63	62...51	49	49
6988	80	79	78...67	65	65
6989	96	95	94...83	81	81
6990	112	111	110...99	97	97
6991	128	127	126.115	113	113
6992	144	143	142...131	129	129
6993	160	159	158...147	145	145
6994	176	175	174...163	161	161
6995	192	191	190...179	177	177
6996	208	207	206...195	193	193
6997	0	0	219...211	210	209

Appendix B: Parameter Numbers and Locations

ID	Parameter Name	Holding Register Number	Holding Register Address	Default Units
1	Temperature	5451	5450	1 = °C
2	Pressure	5458	5457	17 = PSI
3	Depth	5465	5464	38 = feet
4	Level, Depth to Water	5472	5471	38 = feet
5	Level, Surface Elevation	5479	5478	38 = feet
9	Actual Conductivity	5507	5506	65 = µS/cm
10	Specific Conductivity	5514	5513	65 = µS/cm
11	Resistivity	5521	5520	81 = ohm-cm
12	Salinity	5528	5527	97 = PSU
13	Total Dissolved Solids	5535	5534	114 = ppt
14	Density of Water	5542	5541	129 = g/cm^3
16	Barometric Pressure	5556	5555	22 = mmHg
17	pH	5563	5562	145 = pH
18	pH mV	5570	5569	162 = mV
19	ORP	5577	5576	162 = mV
20	Dissolved Oxygen Concentration	5584	5583	117 = mg/L
21	Dissolved Oxygen % Saturation	5591	5590	177 = % Saturation
24	Chloride (Cl^-)	5612	5611	117 = mg/L
25	Turbidity	5619	5618	194 = NTU
30	Oxygen Partial Pressure	5654	5653	26 = torr
31	Total Suspended Solids	5661	5660	117 = mg/L

ID	Parameter Name	Holding Register Number	Holding Register Address	Default Units
32	External Voltage	5668	5667	163 = Volts
33	Battery Capacity (remaining)	5675	5674	241 = %
34	Rhodamine WT Concentration	5682	5681	118 = µg/L
35	Rhodamine WT Fluorescence Intensity	5689	5688	257 = RFU
36	Chloride (Cl^-) mV	5696	5695	162 = mV
37	Nitrate as Nitrogen (NO_3^--N) concentration	5703	5702	117 = mg/L
38	Nitrate (NO_3^-) mV	5710	5709	162 = mV
39	Ammonium as Nitrogen (NH_4^+-N) concentration	5717	5716	117 = mg/L
40	Ammonium (NH_4) mV	5724	5723	162 = mV
41	Ammonia as Nitrogen (NH_3-N) concentration	5731	5730	117 = mg/L
42	Total Ammonia as Nitrogen (NH_3-N) concentration	5738	5737	117 = mg/L
48	Eh	5780	5779	162 = mV
49	Velocity	5787	5786	118 = µg/L
50	Chlorophyll-a Concentration	5794	5793	118 = µg/L
51	Chlorophyll-a Fluorescence Intensity	5801	5800	257 = RFU
54	Blue Green Algae-Phycocyanin Concentration	5822	5821	118 = µg/L
55	Blue Green Algae-Phycocyanin Fluorescence Intensity	5829	5828	257 = RFU
58	Blue Green Algae-Phycoerythrin Concentration	5850	5849	118 = µg/L
59	Blue Green Algae-Phycoerythrin Fluorescence Intensity	5857	5856	257 = RFU
67	Fluorescein WT Concentration	5913	5912	118 = µg/L
68	Fluorescein WT Fluorescence Intensity	5920	5919	257 = RFU

ID	Parameter Name	Holding Register Number	Holding Register Address	Default Units
69	Fluorescent Dissolved Organic Matter Concentration	5927	5926	118 = µg/L
70	Fluorescent Dissolved Organic Matter Fluorescence Intensity	5934	5933	257 = RFU
80	Crude Oil Concentration	6004	6003	118 = µg/L
81	Crude Oil Fluorescence Intensity	6011	6010	257 = RFU
87	Colored Dissolved Organic Matter Concentration	6053	6052	118 = µg/L

Appendix C: Unit IDs

ID	Abbreviation	Units
1	C	Celsius
2	F	Fahrenheit
3	K	Kelvin
Pressure, Barometric Pressure (17-32)		
17	PSI	Pounds per square inch
18	Pa	Pascals
19	kPa	Kilopascals
20	Bar	Bars
21	mBar	Millibars
22	mmHg	Millimeters of Mercury (0 to C)
23	inHg	Inches of Mercury (4 to C)
24	cmH_2O	Centimeters of water (4 to C)
25	inH_2O	Inches of water (4 to C)
26	Torr	Torr
27	atm	Standard atmosphere
Distance/Length (33-48)		
33	mm	Millimeters
34	cm	Centimeters
35	m	Meters
36	km	Kilometer
37	in	Inches
38	ft	Feet
Coordinates (49-64)		
49	deg	Degrees
50	min	Minutes
51	sec	Seconds

Conductivity (65-80)		
65	µS/cm	Microsiemens per centimeter
66	mS/cm	Millisiemens per centimeter
Resistivity (81-96)		
81	ohm-cm	Ohm-centimeters
Salinity (97-112)		
97	PSU	Practical Salinity Units
98	ppt	Parts per thousand salinity
Concentration		
113	ppm	Parts per million
114	ppt	Parts per thousand
115		(Available)
116		(Available)
117	mg/L	Milligrams per liter
118	µg/L	Micrograms per liter
119	---	(Deprecated)
120	g/L	Grams per liter
121	ppb	Parts per billion
Density (129-144)		
129	g/cm3	Grams per cubic centimeter
pH (145-160)		
145	pH	pH
Voltage (161-176)		
161	µV	Microvolts
162	mV	Millivolts
163	V	Volts
Dissolved Oxygen (DO) % Saturation (177-192)		
177	% sat	Percent saturation
Turbidity (193-208)		
193	FNU	Formazin nephelometric units
194	NTU	Nephelometric turbidity units
195	FTU	Formazin turbidity units

Flow (209-224)		
209	ft^3/s	Cubic feet per second
210		(Available - was Cubic feet per minute)
211		(Available - was Cubic feet per hour)
212	ft^3/day	Cubic feet per day
213	gal/s	Gallons per second
214	gal/min	Gallons per minute
215	gal/hr	Gallons per hour
216	MGD	Millions of gallons per day
217	m^3/sec	Cubic meters per second
218		(Available - was Cubic meters per minute)
219	m^3/hr	Cubic meters per hour
220		(Available - was Cubic meters per day)
221	L/s	Liters per second
222	ML/day	Millions of liters per day
223	mL/min	Milliliters per minute
224	kL/day	Thousands of liters per day
Volume (225-240)		
225	ft3	Cubic feet
226	gal	Gallons
227	Mgal	Millions of gallons
228	m3	Cubic meters
229	L	Liters
230	acre-ft	Acre feet

231	mL	Milliliters
232	ML	Millions of liters
233	kL	Thousands of liters
234	Acre-in	Acre inches
	% (241-256)	
241	%	Percent
	Fluorescence (257-2720	
257	RFU	Relative Fluorescence Units
	Low-Flow (273-288)	
273	mL/sec	Milliliters per second
274	mL/hr	Milliliters per hour
275	L/min	Liters per minute
276	L/hr	Liters per hour
	Current (289-304)	
289	µA	Microamps
290	mA	Milliamps
291	A	Amps
	Velocity (305-320)	
305	ft/s	Feet per second
306	m/s	Meters per second

Appendix D: Register Data Formats



The Modbus protocol specification requires any multiple-byte data type to be transmitted in Big Endean order, or most significant byte (MSB) first. In-Situ devices shall use the following register data formats.

Register Data Type Table

ID	Type	Size (registers)	Description
2	Unsigned Short	1	2 bytes, 1 register, MSB first
5	Float	2	4 bytes, 2 registers, IEEE floating point format

ID #: 3113
Revision #: 3
Date: August 24, 2023
Geographic Area: All

Technical Practice Area: Data Science
Technical Practice Leader: Stephen Lehrke
SOP Owner: Heidi Vigil

Foth Infrastructure & Environment, LLC

Standard Operating Procedure

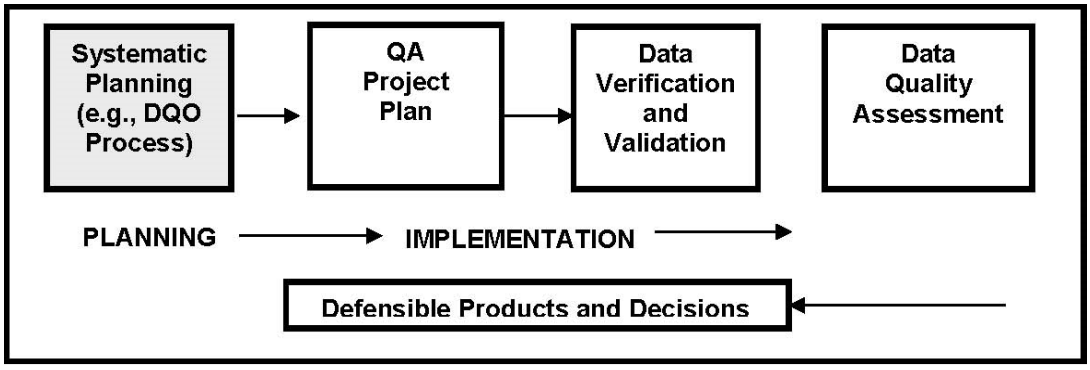
Data Verification, Validation, and Qualification

Introduction

The purpose of this Standard Operating Procedure (SOP) is to establish a procedure for the verification, validation, and qualification of laboratory analytical data. This SOP establishes guidelines for:

1. Reviewing project data quality objectives (DQO) for environmental projects;
2. Selecting the appropriate stage (e.g., Stage 1, 2A, 2B, 3, 4) of analytical laboratory data verification and validation;
3. Selecting the appropriate level (e.g., Level I, II, III, IV) of analytical laboratory data deliverables for the intended stage of data verification and validation;
4. Performing data qualification; and
5. Reporting results and data quality assessment.

This SOP assumes that the DQO process is complete. This SOP can be used during development of a Quality Assurance Project Plan (QAPP) for specifying data quality procedures, or "before, during, and after" environmental sampling programs to aid in selection and execution of data quality procedures.



References

Data Quality Objectives

The following websites provide current guidance for establishing data quality objectives and performing statistical data quality assessments.

U.S. Environmental Protection Agency (USEPA) Superfund Environmental Assessment Quality Assurance Reference Documents website https://www.epa.gov/superfund/search-superfund-documents (accessed 12/04/2019).

USEPA Guidance on Systematic Planning Using the Data Quality Objectives Process. EPA QA/G-4. February 2006. EPA/240/B-06/001.https://www.epa.gov/quality/guidance-systematic-planning-using-data-quality-objectives-process-epa-qag-4.

USEPA Guidance for Data Quality Assessment: Practical Methods for Data Analysis. EPA QA/G-9. July 2000. EPA/600/R-96/084. https://www.epa.gov/sites/production/files/2015-06/documents/g9-final.pdf

USEPA Data Quality Assessment: A Reviewer's Guide. EPA QA/G-9R. February 2006. EPA/240/B-06/002. https://www.epa.gov/sites/production/files/2015-08/documents/g9r-final.pdf

USEPA Data Quality Assessment: Statistical Methods for Practitioners. EPA QA/G-9S. February 2006. EPA/240/B-06/003. https://www.epa.gov/sites/production/files/2015-08/documents/g9s-final.pdf

Data Verification and Validation

The USEPA Superfund Analytical Services Contract Laboratory Program (USEPA CLP) website includes the most current guidance for analytical laboratory data verification and validation: https://www.epa.gov/clp (accessed 11/25/2019).

Historical guidance for laboratory analytical data verification and validation includes the following documents:

USEPA, 2009. Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use, published January 2009. EPA-R-08-005.

USEPA, 2002. Guidance on Environmental Data Verification and Data Validation, EPA QA/ G-8, published November 2002, Part I of IV. EPA/240/R-02/004.

USEPA, 2005. A Compendium of Superfund Field Operations Methods, revised December 2005. EPA/540/P-87/001.

Data Qualification

The USEPA CLP website includes the most current National Functional Guidelines for analytical laboratory data review and qualification data: https://www.epa.gov/clp/superfund-clp-national-functional-guidelines-data-review, and includes the following documents:

USEPA, 2020. National Functional Guidelines for Superfund Organic Methods Data Review, Revised November 2020. EPA-540-R-2017-002.

USEPA, 2020. National Functional Guidelines for Inorganic Superfund Methods Data Review, Revised November 2020. EPA-540-R-2017-001.

USEPA, 2020. National Functional Guidelines for High-Resolution Superfund Methods Data Review, Revised November 2020. EPA-542-B-16-001.

Definitions

Data Review – The process of examining and/or evaluating data to varying levels of detail and specificity. Data review includes verification, validation, and usability assessment.

Verification – Completeness check to confirm that the specified analytical requirements have been met. For the purpose of this guidance, data verification consists of a completeness check to confirm that all data requested from the laboratory have been received and comply with specified requirements.

Validation – Confirmation that the particular requirements for a specific intended use are fulfilled. For the purpose of this guidance, data validation consists of analyte and sample-specific process for evaluating compliance of the laboratory data received with methods, procedures, or contract requirements.

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Personnel Qualifications

None, according to USEPA guidance documents.

Equipment and Supplies

Materials referenced in this SOP include:

- Project planning documents, such as a QAPP, Sampling and Analysis Plan (SAP), or project Work Plan that state project DQO, including performance and acceptance/usability criteria. This SOP assumes that DQO for the project have already been established.
- Analytical laboratory hard copy analytical data deliverables.
- Analytical laboratory electronic data deliverables (EDDs).

Procedures

1. Review the Project DQO to ensure understanding of data type, location, quantity and quality needed to make defensible decisions. The performance and acceptance criteria are established in the project DQO.
2. Select stage of data verification and validation, as established in the Project QAPP. The specifications for each stage of data verification and validation are described below and tabulated in Attachment 1.
    a. Stage 1 – A verification and validation based only on completeness and compliance of sample receipt condition checks is called a Stage 1 Validation. Checks include comparison of reported results against data collection objectives (e.g., sample locations, field quality control [QC] samples, analytical methods, analyte counts, units, reporting limits, etc.), method preservation requirements (e.g., temperature, pH, headspace, etc.), assessment of non-QC laboratory qualifiers (e.g., primary sample holding time, primary sample dilution, etc.), and assessment of transcription or reporting errors.
    b. Stage 2A – A verification and validation based on completeness and compliance checks of sample receipt conditions and ONLY sample-related QC results is called a Stage 2A Validation. Checks include review of instrument performance-related results such as field QC samples (e.g., trip blank [TB], field blank [FB], equipment blank [EB], field duplicate [FD], etc.) and analytical method QC samples (e.g., method blank [MB], laboratory control sample/laboratory control sample duplicate [LCS/LCSD], matrix spike/matrix spike duplicate [MS/MSD], surrogates, etc.).
    c. Stage 2B – A verification and validation based on completeness and compliance checks of sample receipt conditions and BOTH sample-related and instrument-related QC results is called a Stage 2B Validation. Checks include review of instrument tuning-related results such as the number, concentration, and frequency of calibration standards (e.g., initial calibration standards, initial calibration verification [ICV], initial calibration blank [ICB], continuing calibration verification [CCV], continuing calibration blank [CCB], etc.), as well the curves, percent recovery (%R)/difference, equations, calculations, weighting factors, and/or correlation coefficients as appropriate.
    d. Stage 3 – A verification and validation based on completeness and compliance checks of sample receipt conditions, BOTH sample-related and instrument-related QC results, AND recalculation checks (to check for computational errors) is called Stage 3 Validation. Stage 3 Validation requires the use of the laboratory-reported instrument response data to recalculate

calibration windows, analyte retention time, analyte concentration, and instrument performance QC sample recovery (e.g., %R, relative percent difference [RPD], etc.). The results of these recalculations are compared to the results of the laboratory calculations for accuracy.

e. Stage 4 – A verification and validation based on completeness and compliance checks of sample receipt conditions, both sample-related and instrument-related QC results, recalculation checks, AND review of the laboratory raw instrument output, to check for parameterization errors, is called a Stage 4 Validation. Stage 4 Validation requires the use of the laboratory raw instrument output to determine analyte identification and analyte quantitation from analyte-specific characteristics (e.g., column retention time, fluorescence, etc.) expressed as a signal in the raw instrument output. The results of this determination are compared to the laboratory determination for accuracy.

3. Select Level of laboratory analytical data deliverables. The laboratory can provide data at different levels, with each level including increasing amounts of information and detail. The specifications for various levels of laboratory analytical reports are provided in Attachment 2, and detailed below.

   a. Level I – Cover sheet, case narrative, analytical results, sample receiving log, and Chain of Custody. This report is suitable for meeting Stage 1 data verification and validation.

   b. Level II – Level I plus quality control summaries, QC qualifier legend sample summary, lab certification reports, sample analyte count, QC cross-reference table, transfer log. This report is suitable for meeting Stages 1 and 2A data verification and validation.

   c. Level III – Level II plus calibration data, tuning, and check data. This report is suitable for meeting Stages 1, 2A, and 2B data verification and validation.

   d. Level IV – Level III plus instrument run logs, raw data. This report is suitable for meeting Stages 1, 2A, 2B, 3, and 4 data verification and validation.

4. Perform data qualification following procedures as described in National Functional Guidelines documents (USEPA, 2017), and outlined below. Additional guidance regarding analyte, method, and/or instrument-specific qualification, may be found on the Superfund CLP website.

   a. Confirm that all samples planned were collected by looking at the field notes and SAP.

   b. Verify that all sample names and times were documented correctly on the chain-of-custody (COC) and that sample names align with Project planning documents.

   c. Confirm receipt at laboratory within temperature and hold time limits by reviewing COCs and narrative in laboratory analytical report. Any samples that were analyzed out of hold time or temperature limits should be reviewed for potential bias.

   d. Confirm that all samples collected were prepared and analyzed by the correct methods and that complete results were reported.

   e. Evaluate method blanks using the following criteria:

      i. If Reporting Limit (RL)/Practical Quantitation Limit (PQL) is greater than (>) Blank Result > Method Detection Limit (MDL), and

         1. Sample Result is less than (<) RL, then no qualification.

         2. RL/PQL > Sample Result > MDL, then RL qualified with “U.”

         3. Sample Result > RL, then use professional judgment.

ii. If Blank Result > RL, and

1. RL/PQL > Sample Result > MDL, then RL qualified with "U."
2. Blank Result > Sample Result > RL, then report sample result at blank value with "U," or "R" data (for ICB or CCB).
3. 5X Blank Result > Sample Result > RL, then qualify results estimated high "J+," or "R" data (for preparation blank [PB] or MB).
4. Sample Result > Blank Result, then use professional judgment (for ICB or CCB).
5. Sample Result > 5X Blank Result, then no action (for PB or MB).

iii. In general the "5X" stipulation applies to inorganics; organics use a more restrictive criteria of 1X, 2X, 4X, or 5X, depending on the analyte. The functional guidelines should be reviewed for additional details.

f. Evaluate storage, field, or trip blanks using the following criteria:

i. If Blank Result > RL, and

1. Sample Result < RL, then no qualification.

ii. If Blank Result < RL, and

1. Sample Result < RL, then report sample result at RL with "U."
2. Sample Result is greater than or equal to (≥) RL, or 2x Blank Result for methylene chloride, acetone, and 2-butanone, then use professional judgment.

iii. If Blank Result ≥ RL, and

1. Sample Result < RL, then report sample result at RL with "U."
2. Sample Result > RL but < Blank Result, then report at Sample Result with "U" or "R."
3. Sample Result ≥ RL and ≥ Blank Result or ≥ 2x Blank Result for methylene chloride, acetone, and 2-butanone, then use professional judgment.

Field blanks, trip blanks, and equipment blanks help to evaluate evidence of field or lab interference from sample handling, or collection or analytical procedures. If analytes are detected in field blank, results collected same day are considered impacted. Equipment blanks not always necessary, especially if all equipment is dedicated. If there is a detect on an Equipment Blank, samples collected same day are considered impacted. If there is a detect on a Trip Blank, laboratory interference may impact results analyzed on same day.

g. Calculate the RPD between duplicates and parent samples using the attached example RPD calculation. Evaluate duplicate samples using the following criteria:

i. If the analyte concentration of the sample AND duplicate are greater than five times the RL, the RPD should not exceed 20 percent (%). The RPD for specific matrices used during evaluation are 25% for air, 35% for water, and 50% for soil.

ii. If the analyte concentration of the sample OR duplicate is less than five times the RL, the absolute difference between the sample and field duplicate should not exceed the RL.

iii. In the event that either of these criteria are not met, both sample results should be qualified as "J" or "UJ."

iv. According to functional guidelines, less restrictive criteria are acceptable for non-homogeneous soils as follows; the "five times" and "20%" parameters can be switched with "two times" and "35%," respectively.

h. Evaluate LCS/LCSD analyses using the following criteria:

i. If LCS or LCSD recovery for an analyte is above acceptance limits, analyte results in the associated analytical batch are not qualified for non-detects and are "J" qualified for detected results.

ii. If LCS or LCSD recovery for an analyte is below acceptance limits, the analyte results in the associated analytical batch are qualified "UJ" for non-detects and "J" for detected results.

iii. If LCS or LCSD recovery for an analyte is less than 10%, the analyte results in the associated analytical batch are qualified "R" for all results.

i. Evaluate MS/MSD analyses using the following criteria:

i. If either the MS or MSD recovery or the RPD for an inorganic analyte is below acceptance limits, the analyte result for the associated parent sample is qualified "U" for non-detects and "J-" for detected results.

ii. If either the MS or MSD recovery or the RPD for an inorganic analyte is above acceptance limits, the analyte result for the associated parent sample is qualified "U" for non-detects and "J+" for detected results.

iii. If either the MS or MSD recovery or the RPD for an organic analyte is below acceptance limits, the analyte result for the associated parent sample is qualified "UJ" for non-detects and "J-" for detected results.

iv. If either the MS or MSD recovery or the RPD for an organic analyte is above acceptance limits, the analyte result for the associated parent sample is qualified "UJ" for non-detects and "J+" for detected results

v. Results should not be qualified based on non-project specific MS/MSD sample recoveries, or if the concentration of the project-specific MS/MSD sample is greater than 4 times the spike concentration.

j. Apply data qualifiers following the criteria listed in parts 4a through 4h.

The data qualifiers used to qualify analytical results associated with QC parameters outside data quality objectives are defined as:

U = The analyte was not detected above the numerical quantitation limit (i.e., RL).

J = The analyte was positively identified, but the analytical result (i.e., quantitation) is an estimated value.

UJ = The analyte was not detected above the RL, but the RL is an estimated value.

R = The analyte may or may not be present and/or quantifiable due to quality control issues. The analytical result is not usable and should be rejected.

N = The analysis indicates presumptive evidence of the presence of the analyte.

NJ = The analysis indicates presumptive evidence of the presence of the analyte, but the numerical value is an estimated quantity.

Results qualified as "J" or "UJ" are of acceptable data quality and may be used quantitatively to fulfill the DQO of the QAPP, per USEPA guidelines.

5. Summarize the results of the data quality procedures in a deliverable data verification and validation report. The most appropriate form of communicating the results should be discussed with the project manager and technical coordinator.

   Examples of deliverables used to communicate the results of data verification and validation and qualification are provided in Attachments 3 and 4. Attachment 3 provides a simple transmittal form for communicating results that could be used for any stage of data validation and verification, including data qualification. Attachment 4 provides a more comprehensive sample memorandum used for communicating results, developed for use with a Level 2 analytical laboratory report and Stage 2A Validation, including data qualification.

   The deliverable should include an overall data quality assessment relative to the project DQO stating if the data set is usable for the intended purposes of the project.

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Attachment 1
Sample Data Verification Memo

Memorandum

2121 Innovation Court, Suite 100
P.O. Box 5095
De Pere, WI 54115-5095
(920) 497-2500
foth.com

August 30, 2023

TO:

CC:

FR:

RE: Groundwater Monitoring Data Verification – October 2022 (Third Quarter 2022)

Introduction

This summary presents data verification results for groundwater samples collected during the October 2022 monitoring event. The data review was performed in accordance with the procedures specified in the Quality Assurance Project Plan (QAPP) Hydrologic Study (Foth, 2008), United States Environmental Protection Agency (USEPA) Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use (USEPA, 2009), USEPA Functional Guidelines for Organic and Inorganic Data Review (USEPA, 2008 and 2010), and quality assurance and quality control (QA/QC) parameters set by the project laboratory, Pace Analytical (Pace).

Groundwater sampling activities followed industry standards and guidance for the following:

- Sample documentation and chain-of-custody (COC) protocol;
- Sample container requirements;
- QC procedures; and
- QA management, including data management and verification procedures.

Samples were collected and submitted to the laboratory in a manner to obtain data that were representative of site conditions. Laboratory analyses were conducted according to analytical methods described in USEPA and American Water Works Association (AWWA) guidance materials. Field QC samples included in a blind field duplicate (FD), equipment blank (EB), and field blanks (FB). Laboratory QC samples included method blanks (MB), method duplicates (MD), laboratory control sample/laboratory control sample duplicates (LCS/LCSD), and matrix spike/matrix spike duplicate (MS/MSD) samples.

Sample Collection Overview

During this monitoring event, eight groundwater samples were collected and submitted to Pace for the following analysis:

- metals by USEPA Methods 6020, 1631E;
- anions by Methods SM4500, ASTM International (ASTM) D516;

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- cations by USEPA Method 6020; and
- general chemistry by Standard Methods SM2320B, SM5310B, SM2540C, and SM2540D.

Additionally, twelve field QC samples were collected and analyzed as part of the sampling program.

Data Verification, Validation, and Qualification

Data Quality Assessment Overview

The laboratory analytical results were reported by Pace under Sample Delivery Group (SDG) 12345. Laboratory level II reports were received for metals, anions, cations, and general chemistry. These laboratory analytical reports are provided in Attachment 1. These sample results were subjected to a USEPA Stage 2B data verification and validation that included an evaluation of the following QC parameters:

- sample preservation and temperature upon laboratory receipt;
- holding times;
- MB detections;
- MD and relative percent difference (RPD);
- LCS/LCSD recovery and RPD;
- MS/MSD recovery and RPD;
- surrogate recovery (for organic parameters);
- field QA/QC samples and RPD;
- simplified charge balance calculation (for ion balancing); and
- completeness summary.

In addition, data qualification was conducted during data verification and validation. The qualified analytical results are summarized in Table 1.

Data Qualifiers

U = The analyte was analyzed for and was not detected above the numerical quantitation limit (i.e., reporting limit [RL]).

J = The analyte was analyzed for and was positively identified, but the analytical result (i.e., quantitation) is an estimated value.

UJ = The analyte was analyzed for and was not detected above the RL, but the RL is an estimated value.

R = The analyte was analyzed for but may or may not be present and/or quantifiable due to quality control issues. The analytical result is not usable and should be rejected.

N = The analysis indicates presumptive evidence of the presence of the analyte.

NJ = The analysis indicates presumptive evidence of the presence of the analyte, but the numerical value is an estimated quantity.

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Results qualified as “J” or “UJ” are of acceptable data quality and may be used quantitatively to fulfill the data quality objectives (DQOs) of the QAPP, per USEPA guidelines.

Sample Preservation and Temperature upon Laboratory Receipt

Samples were received by the project laboratory per USEPA SW-846, intact, with correct preservation, and at the correct temperature (0 to 6 degrees Celsius [°C]).

Holding Times

Samples were extracted and analyzed within the holding time limits set by the respective analytical methods.

Method Blanks

Method blanks were analyzed at the required frequencies. Target compounds were not detected in the method blanks.

Method Duplicates and RPD

Method duplicate samples were evaluated by the following criteria:

- If the analyte concentration of the sample AND duplicate are greater than five times the RL, the RPD should not exceed 20 percent (%).
- If the analyte concentration of the sample OR duplicate is less than five times the RL, the absolute difference between the sample and FD should not exceed the RL.
- In the event that either of these criteria are not met, sample results should be qualified as “J” or “UJ”.

Method duplicate samples were performed at the required frequency. The RPDs for the method duplicates were within acceptance limits.

LCS/LCSD Recovery and RPD

LCS/LCSD analyses were evaluated by the following criteria:

- If LCS or LCSD recovery for an analyte was above acceptance limits, analyte results in the associated analytical batch were not qualified for non-detects and “J” qualified for detected results.
- If LCS or LCSD recovery for an analyte was below acceptance limits, the analyte results in the associated analytical batch were qualified “UJ” for non-detects and “J” for detected results.
- If LCS or LCSD recovery for an analyte was less than 10%, the analyte results in the associated analytical batch were qualified “R” to all results.

LCS/LCSD analyses were performed at the required frequency. The percent recoveries and RPDs for the LCS/LCSD were within acceptance limits.

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MS/MSD Recovery and RPD

MS/MSD analyses were evaluated by the following criteria:

- If MS or MSD recovery for an analyte was above acceptance limits, the analyte results in the associated analytical batch were not qualified for non-detects and "J" qualified for detected results.
- If MS or MSD recovery for an inorganic analyte was below acceptance limits, the analyte results in the associated analytical batch were qualified "UJ" for non-detects and "J" for detected results.
- If MS or MSD recovery for an organic analyte was below acceptance limits, the analyte results for the project specific MS/MSD sample were subject to qualification.
- Results were not qualified based on non-project specific MS/MSD sample recoveries, or if the concentration of the project specific MS/MSD sample was greater than 4X the spike concentration.

MS/MSD analyses were performed at the required frequency. The percent recoveries and RPDs for the MS/MSD were within acceptance limits, with the following exception.

The MS/MSD for analytical batch MPRP/23070 had recoveries for aluminum in QC sample 12345 that were outside of acceptance limits. The samples associated with this analytical batch that required "J" flags for aluminum are summarized in Table 1.

Field QC Samples

Blank Sample Source Water

The source water that was used for blank samples originated from a drinking water source. As a drinking water it is subject to Minnesota Rule (Minn. R.) 7050 Class I standards, which conform to Code of Federal Regulations (CFR) 40 part 141 and 143 primary (i.e., USEPA maximum contaminant level [MCL]) and secondary drinking water standards.

Subsequently, it is acceptable for this source water to exhibit analytical detections as long as they are below Class I standards. Therefore, interpretation from the blank samples is limited to a qualitative assessment of potential interference (e.g., background, equipment, etc.).

Field Blank

One FB was collected during this monitoring event. The purpose of the FB is to assess the presence of target parameters, originating from background (i.e., field interference), which may contribute to analytical detections in primary samples. The qualitative assessment is a relative comparison of detections in the FB to detections in primary samples. Although the FB had detections of magnesium and total dissolved solids, they were well below the concentrations observed in primary samples. Therefore, it is not likely that magnesium and total dissolved solids, originating from background, contributed to analytical detections in the primary samples. The analytical results of the FB are provided in Table 2.

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Equipment Blank

One EB was collected during this monitoring event. The purpose of the EB is to assess the presence of target parameters, originating from the low-flow sample pump, which may contribute to analytical detections in primary samples. The qualitative assessment is a relative comparison of detections in the EB to detections in the FB.

Although the EB had detections of barium, calcium, copper, magnesium, manganese, nickel, mercury, sodium, total dissolved solids, and zinc, only copper, nickel, mercury, and zinc exhibited concentrations comparable to or in excess of concentrations observed in the FB and primary samples. Therefore, it is possible that copper, nickel, mercury, and/or zinc, originating from the sample pump, could have contributed to analytical detections in the primary samples. The analytical results of the EB are provided in Table 2.

Mercury Field Blanks

Mercury FBs were collected at each monitoring location where a primary mercury sample was collected. The purpose of the mercury FB is to assess the potential for site-specific field interference of mercury, which may contribute to mercury detections in the primary samples. The water used for the mercury blank is laboratory-grade deionized (DI) water, which is analyzed in the laboratory prior to being used as FB water. The analytical results for the ten mercury FBs were below the RL.

Blind Field Duplicate

One FD was collected during this monitoring event. The purpose of the FD is to assess the analytical laboratory instrument precision; specifically, to repeat the same result for a sample collected from the same location at the same time. FDs are evaluated by the same criteria as method duplicates stated above. The RPD between the parent sample (Loc4) and FD (DUP01) indicated that the laboratory conducted analytical procedures with an acceptable degree of precision. The RPD between the analytical results of the FD and the parent sample are provided in Table 2.

Simplified Charge Balance Calculation

As an additional QA/QC measure, a simplified spreadsheet-based charge balance calculation was performed on the laboratory analytical results reported for each sample location. This method does not consider some aspects that may play a role in charge balance calculations, such as complexation with other ions or organic ligands, and other sources of alkalinity other than expressed from carbonate and bicarbonate ions. Therefore, this method is not used to complete a formal charge balance, which typically requires software that numerically solves an aqueous equilibrium modeling problem.

The charge balance error should be small (i.e., less than 10% or 1 milliequivalent per liter [meq/L], whichever is greater) if all the charged species were analyzed and the analyses were completed accurately. For this reason, data for samples reporting larger charge imbalances will generally receive greater scrutiny relative to the reporting of consistent units, transcription errors, and other potential errors. For example a large charge imbalance may result from a major ion not analyzed, an ion concentration entered using incorrect units, or other data entry errors. It is important to note that relative charge balance errors are expected to be higher for

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waters with relatively low ion concentrations. A summary of the charge balance calculations are provided on Table 3.

The charge balance calculations indicated anions and cations were well balanced during this monitoring event. The charge balance error was slightly elevated negative at Loc7 and Loc11 with primary anionic contributions from bicarbonate alkalinity and sulfate. The analyses were considered valid and accurate. In addition, the analytical results were reviewed for reporting errors, and none were detected.

Completeness Summary

Two types of completeness were calculated for this project, namely contract and technical. As specified in the project DQOs, the goal for completeness for the site is 90%. Results indicated as not reportable by the laboratory are not included in the completeness calculations.

The contract completeness included analyte counts for primary samples and secondary samples, including field QC samples. The technical completeness included the protocol and contract deviations for sample preservation, temperature, holding time, method blanks, LCS/LCSD, MS/MSD, and the implications of field QA/QC samples. The contract completeness and technical completeness for all analytes were 100% and 98%, respectively. The completeness summary is provided in Table 4.

Conclusion

The laboratory analytical results have met the project DQOs. The laboratory analytical results are considered representative of site conditions. Based on field and laboratory QA procedures, and data verification and validation, the analytical results are usable for the intended purposes.

References

Foth Infrastructure & Environment, LLC (Foth), 2008. *Quality Assurance Project Plan Hydrologic Study*.

United States Environmental Protection Agency (USEPA), 2009. *Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use*

USEPA, 2008. National *Functional Guidelines for Superfund Organic Methods Data Review*

USEPA, 2010. National *Functional Guidelines for Inorganic Superfund Data Review*

Attachments

Tables

Attachment 1: Laboratory Analytical Reports

SAMPLE

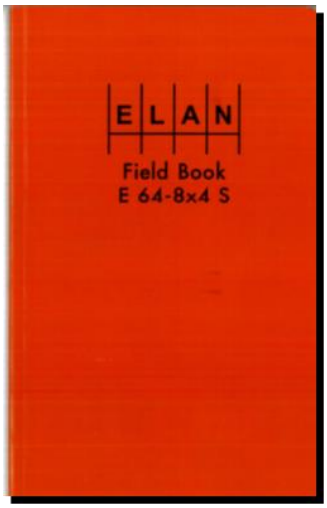
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Standard Operating Procedure

Field Log Book

Introduction

The purpose of this Standard Operating Procedure (SOP) is to set the minimum criteria for content entry and form of a Field Log Book.



A Field Log Book is a bound notebook that is used at field sites and contains detailed information regarding site activities including dates, times, personnel names, activities conducted, equipment used, weather conditions, etc. A Field Log Book is used by a variety of different field personnel and is part of the project file. Each project has its own Field Log Book. They are not to be used for multiple projects with different project identification (ID) numbers.

Foth Infrastructure & Environment, LLC (Foth) gathers information for scientific and engineering evaluations. As part of the information gathering process, Field Log Books are often the sole source for interpretation of information and are legal documents.

The purpose of Field Log Book documentation is to collect information that is not documented in any standard form and that can be used by scientists and engineers to interpret data. Entries show the importance of:

- Data collection objectives;
- Developing and following site specific sampling plans;
- Following regulatory regulations and permits;
- Documenting pre-sampling preparations;
- Changing environmental conditions; and
- Locations and types of forms used in documenting the field work of a project.

A Field Log Book entry is a process of systematic planning for determining the type, quantity, and quality of information collected that is necessary to make well-informed, valid, and defensible scientific and engineering decisions. This process is applicable during all Foth site operations. Additional requirements for documenting Field Log Books are often included in other SOPs and project-specific documentation.

References

None.

Personnel Qualifications

The project manager or designee is responsible for ensuring that project activities are conducted in accordance with this and other appropriate procedures. Project participants are responsible for documenting information in sufficient detail to provide objective documentation (i.e., check prints, calculations, reports, etc.) that meet the requirements of this SOP.

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Equipment and Supplies

- Site-specific plans.
- Bound, 8-inch x 4-inch hard-covered, water-resistant Field Log Book(s). (Also available in soft-cover or Rite-in-the-Rain.)
- Indelible black ink pen.
- Ruler or similar scale.

Procedures

Specifications for the Field Log Book

1. Bound 8-inch x 4-inch book.
2. Cover should have the project name, project ID, and book number.
3. Pages should be consecutively numbered.
4. Table of contents and the signature page should be on page 1.
5. Name, address, and phone number(s) of key field contacts should be on page 1.

Guidelines for Simplifying Entries

1. Enter procedures for the first sample point, and then reference those procedures for subsequent entries on the same day if procedures did not change.
2. To eliminate redundancy, reference other locations if information is available.

Field Log Book Documentation

Each site or operation where field activities are occurring will have Field Log Books. The details of all field activities shall be recorded in a Field Log Book. Multiple Field Log Books may be used depending upon the number of different types of field personnel conducting activities at the site. They are not to be used for multiple projects with different project IDs.

The following requirements must be met when using a Field Log Book:

1. Enter events and entries in chronological order.
2. Record work, observations, quantity of materials, calculations, drawings, and related information directly in the Field Log Book. If data collection forms are specified by an activity-specific work plan, the information on the form does not need to be duplicated in the Field Log Book. However, forms used to record site information must be referenced in the Field Log Book.
3. Ensure information is factual and unbiased. Avoid including opinions and other project work information.
4. Fill up all pages and use both sides of each page. Do not start a new page until the previous one is full or has been marked with a single diagonal line so that additional entries cannot be made.
5. Write in black, indelible ink. Do not write in pencil unless working in wet conditions.
6. Do not erase, blot out an entry, or use white-out (or equivalent). While changes to an entry may be made before it has been signed and dated, care must be taken not to obliterate what was originally written. Indicate deletions by drawing a single line through the material to be deleted, then initial and date the change.

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7. Do not remove any pages from the book.
8. Do not use loose paper and copy into the Field Log Book later.
9. Record sufficient information to completely document field activities.
10. Make sure entries are neat and legible.
11. Draw a diagonal line through the remainder of the final page at the end of the day.
12. Record the following information on a daily basis:
    a. Date and time.
    b. Name of individual making entry.
    c. Description of activity being conducted including well, boring, sampling, location number as appropriate.
    d. Unusual site conditions.
    e. Weather conditions (i.e., temperature, cloud cover, precipitation, wind direction, and speed) and other pertinent data.
    f. Personnel on site (Foth and non-Foth members).
    g. Level of personal protection to be used.
    h. Arrival/departure of site visitors.
    i. Arrival/departure of equipment.
    j. Sample pickup (chain of custody [COC]) form numbers, carrier, time, electronic location of COC).
    k. Start and completion times of borehole/trench/monitoring well installation of sampling activity.
    l. Health and safety issues.
    m. Instrumentation calibration details.
    n. Other equipment used.
    o. Description of SOP followed or other procedures used.
    p. Description and reason of any variations from standard procedures in sampling plan.
    q. Tracking information for analytical sample containers and coolers.
    r. Reference of all standard forms used, COCs, electronic data and its location.
    s. Sample point condition descriptions.
    t. Duplicates and field blank documentation.
    u. Problems and solutions encountered during field activities.

v. Ending calibrations.

w. Delivery and handling of samples.

Entries in the Field Log Book shall be preceded with the time of the observation. The time should be recorded frequently and at the point of events or measurements that are critical to the activity being logged. All measurements made and samples collected must be recorded unless they are documented by automatic methods (i.e., data logger) or on a separate form required by a standard operating procedure. In such cases, the Field Log Book must reference the automatic data record or form.

While collecting samples, note observations such as color and odor of samples collected. Indicate the locations from which samples are being taken, sample identification numbers, the order of filling bottles, sample volumes, and parameters to be analyzed. If field duplicate samples are collected, note the duplicate pair sample identification numbers. If samples are collected that will be used for matrix spike and/or matrix spike/matrix spike duplicate analysis, record that information in the Field Log Book.

A sketch of the station location may be warranted. All maps or sketches made in the Field Log Book should have descriptions of the features shown and a directional indicator. Maps and sketches should be oriented so that north is towards the top of the page.

Other events and observations that should be recorded include (but are not limited to) the following:

1. Changes in weather that impact field activities.
2. Subcontractor activities.
3. Deviations from procedures outlined in any governing documents, including the reason for the deviation.
4. Problems, downtime, or delays.
5. Upgrade or downgrade of personal protective equipment.

Signing and Initialing Requirements for Field Log Book Entries

1. Initial and date each page.
2. Sign and date the final page of entries for each day.
3. Initial and date all changes.
4. Multiple authors must sign out the Field Log Book by inserting the following:

   Above notes authored by:

   _____ (Sign name)

   _____ (Print name)

   _____ (Date)

5. A new author must sign and print his/her name before additional entries are made.

Post-Operation

At the conclusion of each activity or phase of site work, or a complete Field Log Book, the individual responsible for the Field Log Book will ensure that all entries have been appropriately signed and dated and that corrections were made. To guard against loss of data due to damage or disappearance of Field Log

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Books, copies of completed Field Log Books shall be securely stored within the project master file. Field Log Books are stored in project file 14200.

Restrictions/Limitations

Field Log Books constitute the official record of on-site technical work, investigations, and data collection activities. Their use, control, and ownership are restricted to activities pertaining to specific field operations carried out by Foth personnel and their subcontractors. They are documents that may be used in court to indicate and defend dates, personnel, procedures, and techniques employed during site activities. Entries made in the Field Log Book should be factual, clear, precise, and as non-subjective as possible. Field Log Books, and entries within, shall not to be utilized for personal use.

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Standard Operating Procedure

Shipping and Packaging of Non-Hazardous Samples

Introduction

The purpose of this Standard Operating Procedure (SOP) is to establish a standard procedure for packaging and shipping non-hazardous samples. The primary use of this SOP is for the transportation of samples collected onsite to be sent offsite for physical, chemical, and/or radiological analysis. Samples may be coordinated for courier pick-up. Contact the contracting lab for options. The sampler should consider the following options when selecting the appropriate way to deliver samples to the laboratory: potential for sample breakage and loss due to carrier handling practices, potential for sample tampering during shipment, sample delivery time versus sample holding time, ability to maintain chain-of-custody procedures, compliance with any regulatory restrictions or limitations, and carrier pick-up or drop-off stations.

Non-hazardous samples are those that do not meet any hazard class definitions found in 49 Code of Federal Regulations (CFR) 107-178, including materials designated as Class 9 materials and materials that represent Reportable Quantities (hazardous substances).

References

ASTM International (ASTM). ASTM Designation D6911 – 03, *Standard Guide for Packaging and Shipping Environmental Samples for Laboratory Analysis*. 2003.

Code of Federal Regulations (CFR), Transportation (Title 49 CFR Parts 107 – 178). *Hazardous Materials*. https://www.govinfo.gov/content/pkg/CFR-2019-title49-vol2/xml/CFR-2019-title49-vol2-part107.xml

United States Environmental Protection Agency Region 3. *Sample Submission Procedures for the Office of Analytical Services and Quality Assurance (OASQA) Laboratory Branch, Revision 13*. January 19, 2014.

Please refer to the appropriate regulations from the State Department of Transportation (DOT) and/or International Air Transport Association (IATA), and contact the shipping carrier for instructions, if necessary.

Personnel Qualifications

Qualifications of personnel are as directed in the Field Sampling Plan (FSP), Health and Safety Plan (HASP), and appointed by the Project Manager (PM).

Equipment and Supplies

General Equipment

- Shipping container(s);
- Samples;

- Bubble wrap;
- "Quality" cubed ice (not ice from motel ice machine);
- Various types of packing supplies, such as packing tape, permanent inked markers, duct tape, plastic bags (or equivalent, e.g., 33-gallon), etc.;
- 55-gallon bag or appropriate-sized bag for holding ice in shipping container;
- Ziploc® plastic bags or equivalent;
- Custody seals; and
- Chain-of-custody form(s).

Specific Equipment Definitions

- Cooler/Shipping Container – Any hard-sided insulated container meeting any state DOT or IATA's general packaging requirements. The container should be sufficiently large enough to hold a number of sample containers or bottles without exceeding weight limitations.
- Bubble Wrap – Plastic sheeting with entrained air bubbles for protective packaging purposes.
- Temperature Blank – Measured by the contracting laboratory to determine whether site-specific samples have been adequately cooled during shipment and storage.

Procedures

Packaging

1. Follow shipping instructions from contracting lab.
2. Use tape to seal off the cooler drain on the inside and outside to prevent leakage.
3. Place packing material on the bottom of the shipping container (cooler) to provide a soft impact surface. It is recommended to place absorbent materials on the bottom of the shipping container to prevent any potential leakage from the inside.
4. Place a 55-gallon or equivalent plastic bag into the cooler (to minimize the possibility of leakage during transit).
5. Starting with the largest glass container, wrap each container with sufficient bubble wrap to ensure the best chance to prevent breakage of the container. Pack the largest glass containers in the bottom of the cooler, placing packing material between each of the containers to avoid breakage from bumping.
6. Double-bag the ice (chips or cubes) in gallon or quart freezer Ziploc® plastic bags or equivalent, if required, and wedge the ice bags between the sample bottles. (Use "quality" ice, not ice from a motel ice machine.)
7. Add enough ice to sufficiently keep sample temperatures consistently cool during shipment.
8. When sufficiently full, place a laboratory-provided temperature blank inside of the cooler.
9. Seal the inner protective plastic bag, and place additional packing material on top of the bag to minimize shifting of containers during shipment.

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10. Tape a gallon Ziploc® bag or equivalent to the inside of the cooler lid and place the completed chain-of-custody document inside (a copy of the chain-of-custody should be retained by the shipper). The completed original chain-of-custody (retain a copy for record-keeping) should be placed inside a Ziploc bag (or equivalent), to prevent it from becoming wet during shipment, and then should be placed and taped to the inside of the cooler lid. Seal the cooler shut.

11. Place a custody seal on two separate portions of the cooler to provide evidence that the lid has not been opened prior to receipt by the intended recipient.

12. Tape the shipping container (cooler) shut using packing tape, duct tape, or other tear-resistant adhesive strips. Taping should be performed to ensure the lid cannot open during transport. A minimum of three rotations at two points of tape on the cooler is recommended. Tape will be placed in an orientation that covers the custody seals

An alternate method for packaging is as follows:

1. Follow packaging instructions from contracting laboratory.

2. Use tape to seal off the cooler drain on the inside and outside to prevent leakage.

3. Place packing material on the bottom of the shipping container (cooler) to provide a soft impact surface.

4. Open and place a large (e.g., 33-gallon) bag (first bag) inside of the cooler.

5. Use a second bag and pack the sample containers inside of the second bag, placing the containers upright, and the largest containers first. Ensure glass containers are placed in laboratory-provided bubble wrap and sealed before placing them in the second bag.

6. Once the second bag is sufficiently filled with sample containers, tie the second bag (try to get as much air out of the second bag as possible before tying) closed, and carefully place it inside the first bag. The second bag should be sufficiently filled with sample containers that ice will cover and keep the sample containers cool. Be sure not to fill the second bag with too many sample containers as this may prevent some containers from contacting ice. Too many sample containers will also increase the cooler weight, which may create transport issues.

7. Add ice (use purchased ice, not ice from a motel ice machine) to the inside of the first bag. Add enough ice to sufficiently cover the sample containers and keep sample temperatures consistently cool during transportation.

8. Once sufficiently filled with ice, place a laboratory-provided temperature blank container inside of the first bag and tie the first bag shut.

9. Place additional packing material on top of the bag to minimize shifting of containers during transportation. The completed original chain-of-custody (retain a copy for record-keeping) should be placed inside a Ziploc bag (or equivalent), to prevent it from becoming wet during shipment, and then should be placed and taped to the inside of the cooler lid.

10. Place a custody seal on two separate portions of the cooler to provide evidence that the lid has not been opened prior to receipt by the intended recipient.

11. Tape the shipping container (cooler) shut using packing tape, duct tape, or other tear-resistant adhesive strips. Taping should be performed to ensure the lid cannot open during transport. A minimum of three rotations at two points of tape on the cooler is recommended. Tape will be placed in an orientation that covers the custody seals.

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Labeling

1. "This Side Up" arrow must be adhered to all sides of the cooler.

    a. Other recommended labels include: "Fragile" and "Packed in Wet Ice."

2. The name and address of the receiver and the shipper must be on the top of the cooler.

3. The air bill must be attached to the top of the cooler. Applying packing tape to the shipping label is recommended to ensure that the label is not inadvertently removed during shipment.

Shipping

1. If a project has a specific cooler shipment checklist requirement, it shall be completed and kept in the project file. Custody seal numbers may need to be recorded and tracked.

2. It is recommended that the laboratory should be contacted the day samples are expected to be delivered to verify that samples were received and in good condition.

3. Shipping tracking numbers should be kept in the project file and provided to the laboratory upon shipment.

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Standard Operating Procedure

Sample Chain of Custody

Introduction

As part of consulting services, Foth Infrastructure & Environment, LLC (Foth) collects a wide range of environmental samples. All samples collected must be accompanied by a chain of custody when submitted for analysis to ensure proper security and legal handling of samples.

Proper documentation of sample custody is necessary to trace a sample from point of origin through the final report or completion of the project. Requiring samples to have a chain of custody ensures proper security and legal handling of samples as they move between the different parties that are responsible for their collection and analysis. A chain-of-custody form is prepared by completing a chain-of-custody record form (see Foth's form that is attached as an example). Typically, these forms are provided by the laboratory that is providing the sample bottles and analysis. If the laboratory does not supply a form, Foth has a generic chain-of-custody form that can be used. These forms are available as a shared Excel template. Chain-of-custody record forms will be filled out by the sampler(s) at the time of sampling and shipping.

This process is intended to be used for both paper and electronic chain-of-custody forms.

References

None.

Personnel Qualifications

The sampler(s) must be trained in properly filling out chain-of-custody forms.

Equipment and Supplies

- Electronic or paper copy of chain-of-custody form
- Pen

Procedures

Sample chain-of-custody documentation will be prepared by the sampler(s) immediately following the collection of samples. A chain of custody is a legal document. Therefore, it must be completed in pen. Foth also has an electronic chain-of-custody form that can be completed on the computer and printed. However, signatures on both electronic and paper chain-of-custody forms are required and must be in ink. Once completed, the chain of custody paper copy will be placed in the master file. Copies are to be stored electronically in the project file on Project Wise.

Chain-of-custody forms will generally include the following information:

1. A unique chain of custody number.
2. Laboratory shipping address.
3. If using a laboratory chain of custody, use Foth as the company name, including branch office location.

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4. Project contact (in most cases, this will be the lab coordinator).
5. Contact phone number.
6. Project number ID.
7. Project name.
8. Project (site) license number (if applicable).
9. Project state.
10. Name of sampler.
11. Project-identified sample naming convention (unique ID).
12. Sample description.
13. Date sample collected.
14. Time sample collected.
15. Analyses with analytical method requested.
16. Sample matrix.
17. Preservation of samples.
18. Indicate whether or not sample was field filtered.
19. Number of pages (i.e. 1 of 1).
20. Address for where reports should be mailed.
21. Address of where invoice should be sent. Invoices that are not sent to the client's address must be sent to invoices@foth.com per accounting procedures.
22. Regulatory program.
23. Special quality assurance (QA) needs (turnaround time).
24. Any request for data submitted by e-mail or any other format other than printed copy.
25. Laboratory receiving information section completed by the laboratory.
26. Shipping method and tracking numbers.
27. Signature section for transfer of custody with date and time section.

After collection, samples are securely stored and packaged as required by analytical protocol until delivered to the laboratory. The chain-of-custody document remains with the samples during transport and serves as a written record of sample possession and transference. A sample is considered to be in custody if it is in one's possession, is locked and sealed during shipment, or is placed in a secure area limited to authorized personnel. The chain of custody must be signed and dated by everyone who takes possession of the sample. If the electronic chain-of-custody form is used, a minimum of two printed copies must accompany the samples to the laboratory. All copies are signed and dated during sample

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transfer. Laboratory personnel will note any damaged sample containers, or discrepancies between the sample label and information on the chain of custody.

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Attachment 1

Sample Chain-of-Custody Form

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CHAIN-OF-CUSTODY / Analytical Request Document

The Chain-of-Custody is a LEGAL DOCUMENT. All relevant fields must be completed accurately

Page: of **COC Number:** COC-100040

Company: Foth	Report To:	Requested Due Date:	Quote Reference:
Address: 2121 Innovation Court, Suite 100	Copy To:	*TAT:	Project Manager:
De Pere, WI 54115-5095	Invoice To:		Project #:
Phone: Fax: (920) 497-8516	P.O.		Profile #:
Email Address	Project Name:	Regulatory Agency:	Sampling Team Members:
Site License No.:	Project Numbe	State Location:	

Valid Matrix Codes	
Matrix	Code
Soil	SO
Sediment	SE
Surface Water	WS
Wastewater	WW
Groundwater	WG
Ambient Air	AA
Other	X

ITEM NUMBER	SAMPLE ID	MATRIX CODE	SAMPLE TYPE G = Grab C = Composite	DATE COLLECTED MM/DD/YYYY	TIME COLLECTED (Military time)	*Preservatives* # Containers	Unpreserved	H2SO4	HNO3	HCl	NaOH	Na2S2O3	Methanol	Requested Analysis	Filtered (Y/N)	REMARKS / Lab ID
1																
2																
3																
4																
5																
6																
7																
8																
9																
10																
11																
12																

SHIPMENT METHOD	AIRBILL NO.	SHIPPING DATE	NO. OF COOLERS	ITEM #	RELINQUISHED BY / AFFILIATION	DATE	TIME	ACCEPTED BY / AFFILIATION	DATE	TIME

SAMPLE CONDITION:

Temp in C	
Received on Ice	Y / N
Sealed Cooler	Y / N
Sample Intact	Y / N

SAMPLE NOTES:

Additional Comments:

SAMPLER NAME AND SIGNATURE	
PRINT Name of SAMPLER:	
SIGNATURE of SAMPLER	DATE Signed:

Appendix B

Project Variance Contingency Form

Client: _____ Scope I.D.:_____
Project:_____ Page:_____
Prepared by: _____ Date:_____
Checked by:_____ Date: _____

Method Change Contingency Form

Variance No. _____

Date of Issuance: _____ **Effective Date:** _____

Project:	Project No.:	Phase/Task No.:
Prescribed Method:		
New Method:		

Reason for Method Change:

Summarize Method Differences:

Attachments (list documents supporting change):

Technical Practice Leader:	Date:
Project Manager:	Date:
Discipline Lead:	Date:
Received by Field Team or Contractor:	Date:
Received by Agency (if applicable):	Date:

Appendix C

Laboratory Certification and Quality Assurance Manuals

eurofins	Always check on-line for validity.	Level:
Document number: **EFGS-T-AFS-SOP2808**	**Determination of Methyl Mercury in Various Matrices by CV–GC–AFS**	**Standard Operating Procedure**
Old Reference: **EFGS-070**		
Version: **10.1**		Organisation level: **4-Business Unit**
Approved by: **GR8L** Effective Date: **21-JUN-2024**	Document users: **EFGS_SM**	Responsible: **EFGS_SMM**

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DOCUMENT IS NOT CONTROLLED WHEN PRINTED

1) Revision Log:
2) Reference:
3) Cross Reference:
4) Purpose:
5) Scope:
6) Basic Principles:
7) Reference Modifications:
8) Definitions:
9) Interferences:
10) Safety Precautions, Pollution Prevention and Waste Handling:
11) Personnel Training and Qualifications:
12) Sample Collection, Preservation, and Handling:
13) Apparatus and Equipment:
14) Reagents and Standards:
15) Calibration:
16) Procedure:
17) Calculations:
18) Statistical Information/Method Performance:
19) Quality Assurance/Quality Control:
20) Corrective Action
21) List of Attachments

1) Revision Log:

Revision: 10.1	**Effective Date:** This version	
Section	**Justification**	**Changes**
16.3	Updated	Removed picture of manufacturer document from troubleshooting section
19.14	Required	Added instructions for documenting manual integrations to comply with QSM requirements
Appendices	Updated	Removed original appendices A and B (instrument maintenance log and example peak shapes) as both are outdated

Revision: 10	**Effective Date:** 03/07/2024	
Section	**Justification**	**Changes**
Throughout	Required	Changed "monomethyl mercury" to "methylmercury"
Throughout	Required	Changed company to Eurofins Seattle
8	Required	Removed CCVH
8.16	Required	Updated definition
13.1	Required	Updated computer and LIMS requirements
13.10	Required	Removed digestion logbook
14.7.1	Required	Updated concentration and added expiration details
14.8	Required	Added instructions to create methylmercury standard from a salt only if a secondary is not commercially available
15 & 16	Required	Updated ICAL nomenclature for new LIMS system and updated reagent amounts for use of 40 mL vials
15.1	Required	Replace mass with concentration for calibration levels
19.2	Required	Clarified CCV/CCB frequency requirements
19.5	Required	Blank spikes are permissible for LCS/LCSD

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Revision: 10	**Effective Date:** 03/07/2024	
19.11	Required	Added recovery criteria to all calibration points

Revision: 9	**Effective Date:** 01/05/2023	
6.2	Required/Clarification	Reword
8	Required	Original Section 8.20 removed
8.1/7/17/19/9.3/4/18.3	Required/Clarification	Reword
8.6	Required	Added CCVH definition
8.8	Required	blank levels for non-DOD vs DOD
8.13	Updated	MB
9.1	Updated	include PETG
9.6	Required	corrected units
13	Required	added PETG
14.4.7/4.8	Required	updated expiration date
15.1.1/20.4	Required	Redundancy
18.4	Updated	rearranged section
19.3	Updated	spiking levels
19.7	Required/Clarification	CCVH
20.4	Required/Clarification	Original Section 10.4 removed

2) Reference:

2.1 EPA Method 1630 Draft Method. January 2001.

2.2 Bloom, N.S. Ultra-Clean Sample Handling, Environmental Lab 1995, March/April, 20.

2.3 Bloom, N.S. Determination of Picogram Levels of Methyl Mercury by Aqueous Phase Ethylation, Followed by Cryogenic Gas Chromatography with Cold Vapour Atomic Fluorescence Detection. Can. J. Fish. Aq. Sci. 1989, 46, 1131.

2.4 Bloom, N.S.; M. Horvat; C.J. Watras Results of the International Mercury Speciation Intercomparison Exercise. Water Air Soil Pollution 1995, 80, 1257.

2.5 Bloom, N.S.; Crecelius, E.A. Determination of Mercury in Seawater at Sub-nanogram per Liter Levels. Mar. Chem. 1983, 14, 49.

2.6 Bloom, N.S.; Fitzgerald, W.F. Determination of Volatile Mercury Species at the Picogram Level by Low-Temperature Gas Chromatography with Cold-Vapor Atomic Fluorescence Detection. Anal. Chem. Acta. 1988, 208, 151.

2.7 Gill, G.A.; Fitzgerald, W.F. Mercury Sampling of Open Ocean Waters at the Picogram Level. Deep Sea Res. 1985, 32, 287.

2.8 Horvat, M.; Bloom, N.S.; Liang, L. A Comparison of Distillation with Other Current Isolation Methods for the Determination of Methyl Mercury Compounds in Low Level Environmental Samples Part 2, Water. Ana.l Chem. Acta. 1993, 282, 153.

2.9 Liang, L.; Bloom, N.S.; Horvat, M. Simultaneous Determination of Mercury Speciation in Biological Materials by GC/CVAFS after Ethylation and Room Temperature Precollection. Clin. Chem. 1994, 40, 602.

2.10 Bloom, N.S.; Horvat, M.; Watras, C.J. "Results of the International Mercury Speciation Intercomparison Exercise," Wat. Air. Soil Pollut., 1995, 80, 1257.

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2.11 Chemical Hygiene Plan, Eurofins Seattle, current version

2.12 TNI Environmental Laboratory Sector, Vol 1, Management and Technical Requirements, ELV1-2016.

2.13 Department of Defense / Department of Energy Consolidated Quality Systems Manual for Environmental Laboratories, prepared by DoD Environmental Data Quality Workgroup (EDQW) and DOE Consolidate Audit Program (DOECAP) Data Quality Workgroup (DOE-DQW), Version 5.3, May 2019.

2.14 Tekran Model 2700 User Manual and Analytical Guides, Rev 1.01 May 2011.

3) Cross Reference:

Document	Document Title
EFGS-Q-QM-QM5805	QA Manual
EFGS-S-HS-12066	Chemical Hygiene Plan
CA-Q-S-006	Detection and Quantitation Limits
EFGS-Q-QD-SOP2710	Balance Verification, Calibration and Maintenance
EFGS-Q-QD-SOP41510	Volumetric Verification and Pipette and Dispenser Operation and Maintenance
EFGS-S-SB-SOP5139	Cleaning of Sampling Equipment and Bottles for Trace Metals Analysis
EFGS-T-TM-SOP2839	Stock and Prepared Standards
EFGS-S-CS-SOP2794	Ultra-Clean Aqueous Sample Collection
EFGS-T-AFS-SOP2986	KOH/Methanol Digestion of Tissues for Methyl Mercury Analysis
EFGS-T-AFS-SOP2797	Distillation of Aqueous Samples for Methyl Mercury Analysis
EFGS-P-DR-SOP2801	Data Review and Validation and Monthly Logbook Reviews
EFGS-T-AFS-SOP5134	Preparation of Sediments by Acidic KBr Extraction into Methylene Chloride for Determination of Methyl Mercury
EFGS-S-T-SOP2806	Preparation of Tenax- and Carbo-Traps for Methyl Mercury and Dimethyl Mercury Analysis
EFGS-P-SP-SOP2811	Sample Preservation and Splitting for Trace/Specialty Metals
EFGS-S-HS-SOP2991	Waste Disposal Procedure for Client Sample Waste

4) Purpose:

4.1 This Standard Operating Procedure (SOP) is designed to ensure that reproducible and traceable procedures are followed in the standardization of the methylmercury (MHg) analyzers and in the analysis of samples for methylmercury, as well as to establish the bounds wherein data will be considered acceptable.

5) Scope:

5.1 This SOP provides for the determination of methylmercury (CH_3Hg) in a wide range of matrices including, but not limited to, aqueous, biological, and geological media. Methylmercury is measured by Cold Vapor-Gas Chromatography-Atomic Fluorescence Spectrometry (CV-GC-AFS) and is calculated by comparing the instrument response of samples to that of standards.

5.2 This method is designed for the determination of methylmercury in the range of 0.05-4.0ng/L (ppt) or 0.05-5.0 ng/g (ppb). Application may be extended to higher levels by selection of a smaller sample size, as long as the instrument value (intensity) remains within the calibration curve.

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6) Basic Principles:

6.1 All aqueous samples should be prepared according to *EFGS-T-AFS-SOP2797*. Sediments/soils are prepared by *EFGS-T-AFS-SOP5134*. Tissues are prepared by *EFGS-T-AFS-SOP2986*.

6.2 An aliquot of prepared sample is adjusted with acetate buffer and ethylated in a closed purge vessel by the addition of sodium tetraethyl borate ($NaBEt_4$). The volatile Hg^0 and ethyl derivatives of CH_3Hg and labile Hg(II) (methyl ethyl and diethyl methyl mercury) are purged from solution by purging with argon onto a graphitic carbon (Carbotrap®) or adsorptive polymer (Tenax®) trap. This trap is dried and then placed into an analytical train and the analytes are thermally desorbed from the trap into an inert gas stream. They are then separated by a GC column, passed through a pyrolitic column (which converts the organomercury forms to detectable elemental mercury) and then into the cell of a Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) for detection. Peak height is measured with a strip chart recorder, or captured electronically, and all results are entered into an excel spreadsheet.

6.3 For dissolved CH_3Hg, samples are filtered through a 0.45-µm capsule filter prior to distillation.

7) Reference Modifications:

7.1 No significant modifications were made to this method.

8) Definitions:

8.1 Analytical Run – the continuous analysis of one or more batches. An analytical run requires a minimum of a 5-point calibration curve, ICV/OPR, ICB, and CCV/CCB every ten samples. An analytical run *must* conclude with an OPR/CCB.

8.2 Batch – no more than 20 client samples grouped for preparation. A batch consists of 3 preparation blanks, 1 LCS/LCSD, and 1 MS/MSD are prepared *per 10* samples.

8.3 Calibration Standards (CAL) – a series of standards that will be used to calibrate the instrument, made from a PDS. A calibration blank plus at least five different concentrations are required, beginning with one at PQL concentration.

8.4 Certified Reference Material (CRM) – a standard of known composition that is certified by a recognized authority and representing a sample matrix. It is used to verify the accuracy of a method.

8.5 Control Limit (CL) – the limit of the range of acceptability for the quality control samples

8.6 Initial Calibration Verification (ICV/OPR) – a standard used to check initial calibration and is prepared from a SDS. This standard is run at mid-level concentration and verifies instrument calibration. It is always followed by an ICB.

8.7 Initial and Continuing Calibration Blank (ICB and CCB) for evaluation of instrument drift, sensitivity, and contamination. ICB must be analyzed directly after the ICV, and the CCBs every 10 samples immediately after CCVs. ICB and CCBs must individually be less than one-half of the Practical Quantitation Limit for non-DOD work and less than one-half of the Practical Quantitation Limit for DOD work only.

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8.8 Laboratory Control Sample and Laboratory Control Sample Duplicate (LCS and LCSD) – a sample containing a known concentration of methyl mercury that is used to monitor complete method performance. The preferred LCS is a matrix matched Certified Reference Material (CRM), but a blank spike meets the requirement as well. In LIMS, the LCS is always referred to as a Blank Spike (BS).

8.9 Method Duplicate (MD) – a second separate sample, taken from the same source sample and analyzed in the laboratory separately at the request of the client.

8.10 Matrix Spikes and Matrix Spike Duplicates (MS/MSD): The purpose of analyzing matrix spikes and matrix spike duplicates (MS/MSD) of a matrix representative sample per each batch is to demonstrate the performance of the analytical method in a particular sample matrix, and to recognize matrix interference. To prepare a MS/MSD for MMHg, predetermined quantities of the analyte are added to a sample matrix before distillation of samples.

8.11 May: This action, activity, or procedural step is optional.

8.12 May Not: This action, activity, or procedural step is prohibited.

8.13 Method Blank (MB) or Preparation Blank (PB): Method blanks consist of the same reagents used to digest the samples, in the same volume or proportion, and are carried through the complete sample preparation and analytical procedure.

8.14 Method Detection Limit (MDL) – the limit derived from an exercise as described in 40 CFR, Part 136, Appendix B. The exercise produces a defined value that is the minimum concentration that can be measured and reported with 99% confidence that the analyte concentration is greater than zero from a given matrix.

8.15 Ongoing Precision and Recovery (OPR) – a standard that is prepared from a secondary source stock standard. This standard is analyzed at 0.5 ng/L and verifies instrument calibration.

8.16 Practical Quantization Limit (PQL) – the minimum concentration that can be reported quantitatively (also referred to as the LOQ, or limit of quantification). The PQL is often described as 1-10 times higher than MDL. The PQL is the upper Control Limit for the ICB, CCB, and MBLK (Prep blank); i.e. these QC standards must be lower in concentration than PQL. In LIMS, the PQL is given the term RL.

8.17 Primary Dilution Standard (PDS) – a standard that is used to make a series of calibration standards for this method.

8.18 Quality control sample (QCS)—A sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process. This sample is analyzed within a batch as an LCS.

8.19 Secondary Dilution Standard (SDS) – a sample of standard from an alternate SSS, used to prepare the ICV, CCV, MS, and MSD standards, and for IDOC/CDOC.

8.20 Shall: This action, activity, or procedure is required.

8.21 Should: This action, activity, or procedure is suggested, but not required.

8.22 Stock Standard Solution (SSS) – a standard of analyte purchased from a certified source for the preparation of working standards.

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9) Interferences:

9.1 Only clean fluoropolymer, borosilicate glass containers, with fluoropolymer line caps or Polyethylene terephthalate glycol (PETG), should be used for samples, standards, and reagents, because Hg vapors can diffuse into, or out of other materials, resulting in results that are biased high or low.

9.2 BrCl will oxidize nearly all forms of mercury. Therefore, pipettes used to aliquot BrCl should never be used for methyl mercury analysis.

9.3 Samples preserved with nitric acid (HNO_3) cannot be analyzed for methyl mercury as the analyte is partially decomposed in the distillation step by this reagent. Special care should be taken when sharing glassware with the Trace Metals group to ensure that all traces of nitric acid have been rinsed from the labware prior to use for standard or reagent creation or storage. It is generally good lab practice to avoid the use of any ICPMS labware for methyl mercury.

9.4 Methyl mercury analysis is pH sensitive and distillation can cause acidification of samples. It is essential that the pH of the distillates be adjusted by the addition of acetate buffer.

9.5 Distilled methyl mercury results are corrected using an empirically derived efficiency factor. This factor is based upon historical data that reflects methyl mercury losses inherent to this procedure.

9.6 Free chlorine interferes and must be removed using ascorbic acid.

10) Safety Precautions, Pollution Prevention and Waste Handling:

10.1 Personnel will don appropriate laboratory attire according to Chemical Hygiene Plan (CHP) *EFGS-S-HS-12066*. This may include, but is not limited to: laboratory coat, apron, eye protection, face shield and protective gloves.

10.2 The toxicity or carcinogenicity of each laboratory reagent has not been fully established. Therefore, every chemical must be treated as a potential health hazard. Exposures shall be reduced as much as possible. Analysts and technicians are expected to familiarize themselves with the characteristics and risks of each chemical they work with by referring to the SDS located at: https://msdsmanagement.msdsonline.com/company/5c1df5b3-747d-4789-8104-42457dc3a3e5/

10.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease-causative agents. Eurofins Seattle will reimburse the expense of Hepatitis A and B immunizations for any laboratory staff member who desires this protection.

10.4 Sodium tetraethyl borate is toxic, gives off toxic gases (triethylboron) and is spontaneously combustible. To discard unused portions of ethylating agent and empty bottles, place into a large beaker of 1N HCl in the fume hood. Triethylboron will bubble off to the air where it is eventually oxidized to harmless boric acid. Boil the acid down to ½ volume to destroy residues before discarding as acid waste.

CAUTION: Fill empty tetraethyl borate vial and cap quickly with water and gently place in specified waste beaker in fume hood. Tetraethyl borate can spontaneously combust upon contact with air.

10.5 Chronic Hg exposure may cause kidney damage, muscle tremors, spasms, personality changes, depression, irritability, and nervousness. Organo-mercurials may cause permanent brain damage. Because of the toxicological and physical properties of CH_3Hg, pure standards should be handled only

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by highly trained personnel thoroughly familiar with handling and cautionary procedures and the associated risks.

10.6 It is recommended that the laboratory purchase a dilute standard solution of CH_3Hg for this method. If primary solutions are prepared, they shall be prepared in a hood, and a NIOSH/MESA-approved toxic gas respirator shall be worn when high concentrations are handled.

10.7 Facility—when samples known or suspected to contain high concentrations of CH_3Hg are handled, all operations (including removal of samples from sample containers, weighing, transferring, and mixing) should be performed in a glove box demonstrated to be leak-proof, or in a fume hood demonstrated to have adequate airflow. Gross losses to the laboratory ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazard except in an accident.

10.8 Personal hygiene – hands and forearms should be washed thoroughly after each manipulation and before breaks (coffee, lunch, and shift).

10.9 Effluent vapors – the effluent from the CV-AFS should pass through either a column of activated charcoal or a trap containing gold or sulfur to amalgamate or react with Hg vapors.

10.10 See Eurofins Seattle Chemical Hygiene Plan (CHP) for general information regarding employee safety, waste management, and pollution prevention.

10.11 Pollution prevention information can be found in the current Eurofins Seattle Chemical Hygiene Plan (CHP), which details and tracks various waste streams and disposal procedures.

10.12 All laboratory waste is accumulated, managed, and disposed of in accordance with all federal, state, and local laws and regulations. Any waste generated by this procedure should be disposed of according to *EFGS-S-HS-SOP2991* (waste disposal), which provides instruction on dealing with laboratory and client waste.

11) Personnel Training and Qualifications:

11.1 An analyst must perform an initial demonstration of capability (IDOC) that includes four replicates of a secondary source before being qualified to analyze samples without supervision. Continuing DOC will be maintained and monitored via performance on CRMs and other QC samples, as well as obtaining acceptable results on proficiency testing exercises.

11.2 Training is documented by the employee and supervisor, and is kept on file in the QA Office. The employee must read, understand, and by signing the training document, agree to perform the procedures as stated in all Standard Operating Procedures (SOPs) related to this method.

11.3 All employees must read the Quality Manual (*EFGS-Q-QM-QM5805*) and complete the annual Ethics training.

11.4 All training documents including IDOCs, CDOCs, Initial QA orientation, and Ethics training are stored by the Quality Assurance Manager in the employees training file for ten years after the employee is no longer working for Eurofins Seattle.

11.5 Chemical Safety Training, Compressed Gas Training, Chemical Hygiene Plan documentation, and Shipping of Hazardous goods, are stored by the Health and Safety Officer for ten years after the employee is no longer working for Eurofins Seattle.

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12) Sample Collection, Preservation, and Handling:

12.1 Samples are collected into rigorously cleaned fluoropolymer bottles (with fluoropolymer caps), Polyethylene terephthalate glycol (PETG), or borosilicate glass bottles with fluoropolymer lined caps. Bottles should be tightly sealed, and care must be taken to minimize headspace within the sample bottle. Acid preserved samples are stable for at least six months, if kept in the dark and cool.

12.2 Collect samples using clean sampling techniques, according to *EFGS-S-CS-SOP2794*.

12.3 Freshwater samples are preserved to 0.4% HCl. Saline samples are preserved to 0.2% H_2SO_4. See *EFGS-P-SP-SOP2811* (sample preservation). Samples may be shipped to the laboratory unpreserved if they are (1) collected in appropriate bottles, (2) filled to the top with no head space, capped tightly, and (4) maintained at 0-4°C from the time of collection until preservation. The samples must be acid-preserved within 48 hours of sampling.

12.4 After preservation, aqueous samples are stored in a secure refrigerator until distillation. After distillation, aqueous samples are stored in the walk-in refrigerator until disposal. Tissue and sediment samples are stored in a secured, designated freezer before and after preparation.

13) Apparatus and Equipment:

13.1 LIMS – TALS (current production version); Computer equipped with Windows 10 (or higher) and with MS Excel.

13.2 Nitrogen (N_2): Grade 4.5 (standard laboratory grade) nitrogen, which can be further purified of mercury using a gold or iodated carbon trap located in line between the gas output and the analyzer gas input.

13.3 Argon (Ar): No less than Grade 4.7 (high purity grade) argon that has been further purified by the removal of mercury using a gold or iodated carbon trap that is located in line between the gas output and the analyzer gas input.

13.4 Pipettes: Calibrated variable pipettes with a range of 10 µL – 5 mL. Used to make solutions and sample dilutions. Pipettes are to be calibrated weekly according to *EFGS-Q-QD-SOP41510*.

13.5 Analytical balance - capable of accurately weighing to the nearest 0.0001 g, calibrated according to *EFGS-Q-QD-SOP2710*. The balance must have been calibrated earlier in the date and a calibration sticker shall be in place on the balance.

13.6 Volumetric flasks - class A and cleaned according to *EFGS-S-SB-SOP5139*. Make sure to use volumetric flasks designated for methyl mercury use only. These flasks should be filled with MQ and preserved with 5% HCl if they are not to be used immediately after cleaning.

13.7 Glass bottles: Borosilicate glass bottles can be used to store samples, standards and reagents.

13.8 Tekran 2700 with autosampler: Automated MHg system that utilizes the purge and trap system. See Instrument Software Inventory *EFGS-S-IT-WI7061*.

13.9 Teflon (Fluoropolymer) bottles: Teflon bottles that have been cleaned for methyl mercury use can be used to make and store the Acetate Buffer and to store standards and samples.

13.10 CV-GC-AFS instrument Log

13.11 Polyethylene terephthalate glycol (PETG) - Bottles that have been rinsed for methyl mercury use can be used to make and store the Acetate Buffer and to store standards and samples.

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14) Reagents and Standards:

14.1 Reagent Water: 18-MO ultrapure deionized water starting from a pre-purified (distilled, R.O., etc.) source is used. To remove any remaining trace metals and organics, an activated carbon cartridge is placed between the final ion exchange bed and the 0.2-µm filter. The reagent water is tested for trace metal and mercury concentrations on a weekly basis and must test less than the PQL to be in-control.

14.1.1 This is used to rinse all pipette tips prior to analysis.

14.2 Hydrochloric acid: Trace-metal purified reagent HCl containing less than 5 pg/mL Hg. CH_3Hg is not stable in concentrated acid, so the acid does not need to be tested for this analysis. The acid used at Eurofins Seattle shall be lot sequestered and tested below 5 pg/mL Hg prior to being used. The acid is entered into LIMS with an expiration date of three years and a copy of the Certificate of Analysis (CoA) shall be on file with the Quality Assurance department.

14.3 Sulfuric acid: Trace-metal purified reagent H_2SO_4 containing less than 5 pg/mL Hg. CH_3Hg is not stable in concentrated acid, so the acid does not need to be tested for this analysis. The acid used at Eurofins Seattle shall be lot sequestered and tested below 5 pg/mL Hg prior to being used. The acid is entered into LIMS with an expiration date of three years and a copy of the Certificate of Analysis (CoA) shall be on file with the Quality Assurance department.

14.4 Methyl Mercury Stock and Prepared Standards:

14.4.1 See SOP *EFGS-T-TM-SOP2839* for information regarding the receipt, documentation, preparation, and storage of purchased and prepared standards used by Eurofins Seattle.

14.4.2 Methyl Mercury Stock Solutions are purchased from Absolute Standards (100 ug/mL Hg, Primary) and Alfa Aesar (799 ug/mL Hg, Secondary). Alternate vendors may be used, providing that one primary and at least one secondary source are used.

14.4.3 Spiking Standard, 1000 ng/mL: a PDS made from Primary Stock Standard. Use 1.0 mL of the stock standard into 100 mL reagent water containing 0.5% Glacial Acetic and 0.2% HCl. Expiration date is currently set at 12 months or when the stock standard expires, whichever is shorter. Test this standard by making a 1000X dilution, and then placing 100 µL into an assumed aliquot of 50 mL. Enter 1000 into the Dilution column in the excel spreadsheet. The true value is 2000 ng/L.

14.4.4 Spiking Standard, 100 ng/mL: a PDS made from Primary Stock Standard. Use 0.100mL of the stock standard into 100mL reagent water containing 0.5% Glacial Acetic and 0.2% HCl. Expiration date is currently set at 12 months or when the stock standard expires, whichever is shorter. Test this standard by making a 100X dilution, and then placing 100µL into an assumed aliquot of 50 mL. Enter 100 into the Dilution column of the excel spreadsheet. The true value is 200 ng/L.

14.4.5 Spiking Standard, 10 ng/mL: a PDS made from Primary Stock Standard. Use 0.010mL of the stock standard into 100mL reagent water containing 0.5% Glacial Acetic and 0.2% HCl. Expiration date is currently set at 12 months or when the stock standard expires, whichever is shorter. Test this standard by making a 10X dilution, and then placing 100 µL into an assumed aliquot of 50 mL. Enter 10 into the Dilution column of the excel spreadsheet. The true value is 20 ng/L.

14.4.6 Calibration Standard, 1.0 ng/mL: made from the 100 ng/mL PDS: Use 2.5 mL of the 100 ng/mL standard to 250 mL of reagent water containing 0.5% Glacial Acetic and 0.2% HCl. Expiration date is currently set 1 day.

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14.4.7 Calibration Standard, 0.05 ng/mL: made from the 100 ng/mL PDS (Absolute): Use 0.125 mL of the 100 ng/mL standard to 250 mL of reagent water containing 0.5% Glacial Acetic and 0.2% HCl. This standard may also be used for the BS/BSDs and MS/MSDs if a lower spike level is desired. Expiration date is currently set 1 day.

14.4.8 Initial Calibration Verification, 0.5 ng/mL: made from SDS): Made as a dilution of the secondary source preserved at 0.5% glacial acetic acid and 0.2% HCl.

14.5 Ethylating Agent: **CAUTION:** Sodium tetraethyl borate is toxic, gives off toxic gases (triethylboron) and is spontaneously combustible. To discard unused portions of ethylating agent and empty bottles, place into a large beaker of 1N HCl in the fume hood. Triethylboron will bubble off to the air where it is eventually oxidized to harmless boric acid. Boil the acid down to ½ volume to destroy residues before discarding as acid waste.

14.5.1 Procedure: Locate the 125 mL Teflon ethylating agent bottle in freezer in the methyl lab. Rinse bottle 3X with reagent water. Fill bottle with 100 mL of reagent water. Add 2 g reagent grade KOH. Shake vigorously until the KOH pellets have completely dissolved. Put solution in the freezer and leave to cool until crystals just start to form. Meanwhile, gather about 15 of the 5 ml ethylating agent (PTFE) vials and dump the used ethylating agent into an appropriate waste contained and. Rinse the vials and let them dry under the clean hood on new blotter paper. Remove crystallized KOH solution from the freezer and place in hood. Open tetraethyl borate vial with a new razor blade and wipe off excess wax before removing cap. Upon opening, immediately pour the contents of the tetraethyl borate vial into the KOH solution. **CAUTION:** Fill empty tetraethyl borate vial and cap quickly with water and gently place in specified waste beaker in fume hood. (Sodium Tetraethylborate can spontaneously combust upon contact with air). Shake the 125 mL Teflon bottle well and then pour into dry 5 ml PTFE vials (fill 2/3 to 3/4 full). Cap and freeze the vials until needed. If any doubt arises about the quality of the ethylating agent, make a new batch, as the old material often gives good results for standards, but not for environmental samples. Do not use $NaBEt_4$ solid or solutions if they have a yellow color.

14.5.2 Ethylating agent is identified by the lot number of the solid reagent (see section 9.1.3 for entering neat reagents). The solution shall be stored in freezer.

14.6 Acetate Buffer: Fill a 1 L bottle ¾ full with reagent water. Add 272 g of sodium acetate and 120.1 g acetic acid (2 moles). Shake to dissolve and bring to a final volume of 1L with water. Then, add 0.5 ml ethylating agent and quickly shake and let sit about 20 minutes. Purge with nitrogen or argon overnight. The reagent shall be entered into LIMS.

14.6.1 Acetate Buffer is given a default expiration of six months, or the expiry of the parent reagents, whichever is sooner.

14.6.2 Acetate buffer is tested by ethylating 600 uL of reagent during an analytical run. The default aliquot entered into the Excel file is 50 mL. The warning limit for the ethylating agent is 0.025 ng/L. If the reagent tests above the control limit, it can be re-purged or remade prior to retesting. Only one analytical replicate is necessary.

14.7 L-Ascorbic Acid: reagent grade

14.7.1 2.0% Ascorbic acid: Add 0.4 g L-Ascorbic acid to 20 mL of reagent water. This solution has a two-week expiration date or expires when the L-Ascorbic acid does (whichever is sooner).

14.8 Secondary stock standard (from salt): a secondary source standard may be prepared from a salt if no other liquid standards are available from other commercial vendors with appropriate certifications. An approximately 1000 ppm solution should be prepared in a volumetric flask, using 0.5% v/v acetic acid/0.2% v/v hydrochloric acid as the diluent. Heating for an hour (at 50 C) and settling overnight or sonication may be necessary to dissolve the salt.

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14.8.1 The concentration of this solution is determined through oxidation with 0.2N bromine monochloride. Seven dilutions of this standard (10-fold) are created using 0.2N bromine monochloride as the diluent and are allowed to oxidize overnight. These dilutions are analyzed for total mercury by method 1631E. Two replicates of the stock solution (not oxidized) are analyzed by 1631E as well to estimate the ionic mercury concentration of the stock solution (diluent must be water for analysis). The difference between the average oxidized and average not oxidized concentrations is taken as the methylmercury concentration of the stock standard per method 1630.

15) Calibration:

15.1 The calibration sequence determines the range of sample concentrations that are reportable. The calibration sequence starts with the instrument blank level (IBL) followed by a minimum of a 5-point curve using the methyl mercury calibration standard solutions. Suggested calibration points are: 0.05 ng/L, 0.20 ng/L, 1.0 ng/L, 2.0 ng/L, and 4.0 ng/L.

15.2 Immediately following the standard calibration curve, an Initial Calibration Verification (ICV/OPR) standard is analyzed. The ICV/OPR standard is made from a secondary source (see section 14.3.8). Following the ICV/OPR, an Initial Calibration Blank (ICB) is analyzed.

15.3 To calibrate the MHg 2700 instrument setup, follow the protocols below:

15.3.1 Ensure instrument and computer have been powered up. The system should be on for 30 minutes before calibration analysis is started.

15.3.1.1 Open the software of the instrument with the short cut on the desktop.

15.3.1.2 Open a new worksheet under the EPA 1630 method.

15.3.2 While the system is stabilizing grab eight of septa vials and label them with IBL, STD1, STD2, STD3, STD4, STD5, ICV, ICB

15.3.3 Add approximately 30 mL reagent water to each vial.

15.3.4 Add an appropriate amount of calibration standard to each vial.

15.3.4.1 If using the suggested points above, 30 µL of 0.05 ng/mL solution is added to CAL1, 120 µL of 0.05 ng/mL solution is added to CAL2, 30 µL of 1.0 ng/mL solution is added to CAL3, 60 µL of 1.0 ng/mL solution is added to CAL4, and 120 µL of 1.0 ng/mL solution is added to CAL5.

15.3.5 Add 360 µL of acetate buffer and 30 µL of 2.0% ascorbic acid to each vial. Ensure the solution level is far enough away from the probe inlet at the top of vial (approximately 2 centimeters).

15.3.6 The ICB and IBL only contain water, buffer, ascorbic acid, and ethylating agent.

15.3.7 Remove ethylating agent from the freezer, and check to insure that the liquid to ice ratio is approximately 50%. Add 40.0 µL of the ethylating agent to each vial, immediately returning the ethylating agent to the freezer. Seal and ***vigorously shake*** vials right after the ethylating has been added to each (best to have someone open and cap vials as ethylating agent is being added).

15.3.8 After 30 minutes the system is allowed to start analyzing, Ensure that each vial is placed into the autosampler in consecutive order. Enter the vials into the software as IBL,

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STD1, STD2 and so on. Reference the location of each in the software. The system should start off with a clean cycle.

15.3.9 To start the run click on run worksheet. For the initiation of the run the "run worksheet" portion should be selected with method "clean" for cleans and "psample10" for sample analysis. Click ok and the run with commence. Each clean with take 6 minutes and each sample analysis will take 10.5 minutes.

15.3.10 The instrument will evaluate the each peak and determine speciation of the peaks as well. The integration of the peaks in reported on the worksheet.

15.3.11 The system will stop if no sample IDs are placed in the next row for analysis.

16) Procedure:

16.1 Instrument Start Up (Automated Tekran 2700)

16.1.1 Ensure the instrument has been on for one hour to stabilize before running calibration curve. If instrument was left on overnight no waiting period is necessary.

16.1.2 Open the Tek MDS software on the computer. Evaluate the PG2 reading to be ~7.5 psig and the PG3 reading to be ~15 psig.

16.1.3 On the front of the instrument ensure the status of the five icons (General System, Tekran USB, Detector, Syringe and Liquid Detector) to be within operational requirements.

16.1.3.1 General System icon is the form of a computer and should be green or yellow.

16.1.3.2 Tekran USB icon is the universal USB symbol and should be green.

16.1.3.3 Detector icon is the letter "D" with an arrow under it pointing right and should be green.

16.1.3.4 Syringe icon is a syringe plunger and should be red. The syringe function of the instrument has been disable.

16.1.3.5 Liquid Detector icon is a water drop and should not be present on the display.

16.1.3.6 If any of these icons are not the color indicated then there is an issue with the instrument and this should be investigated before the instrument is used.

16.2 Analyzing Samples

16.2.1 Grab 40 mL VOA vials for each samples/batch QC.

16.2.2 Label each vial with the unique LIMS sample ID.

16.2.3 Pour the prepared sample into the 40mL septa vial. Add 30µL of the 2.0% ascorbic acid and 360 µL of the acetate buffer to the sample. Shake and let sit for 5 minutes.

16.2.4 Add 40µL of the ethylating agent and immediately cap the vial. Shake the contents vigorously immediately and let sit for 30 minutes before analysis.

16.3 Troubleshooting

16.3.1 The following is a summary of common troubleshooting techniques. This is not an all-inclusive list of what may be done to deal with analytical issues. Consultation with the group

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leader is preferred when performing these corrective actions. Analysts are encouraged not to rely on this guideline. Instead, this document should be used as a learning tool. Analysts should be actively striving to learn about troubleshooting as well as creative, productive ways of dealing with analytical issues.

Issue	Usually Identified by:	Potential resolution/investigation
Poor calibration curve (the first time)	Poor Relative Standard Deviation (RSD) control limit >15%	-Halt analysis. Investigate. -First, determine if there was any physical reason why the curve may have failed. (i.e., poor connections, improper pipette techniques, fluctuations in gas flow, etc.). -If there is one point in the curve that skews the rest of the points, rerun this point and name it SEQ-CAL6. -If the poor curve is not due to one standard, but to several, the curve must be reanalyzed.
Failing CCV/CCB	Analyte detect in CCB or poor CCV standard recovery	-Halt analysis. Investigate. -Check all physical possibilities (see calibration failure). -Rerun 2 replicates of failed CCB or CCV. Both must pass to continue analysis. If any fail, instrument must be recalibrated.
Poor analytical accuracy recoveries	MS/MSD recoveries outside control limits	-Determine if samples are qualifiable with QA flow charts (may require checking physical sample if homogeneity is a concern). Follow the Qualifier Flow Charts to see if reanalysis is necessary, or if result may be qualified. -Check all physical possibilities. Check calculations. -Rerun MS/MSD again, ideally at the same aliquot, if possible (but reserving volume for further reanalysis, if this second set fails). -If recoveries are good, consider it good. (Most likely a physical reason that was not observed at the time and could not be noticed after the fact) -If recoveries are poor, run an as/asd within the batch to fulfill QC requirements.
Poor analytical precision	Failing method duplicates or MS/MSD RPD	-Determine if samples are qualifiable with QA flow charts (may require checking physical sample if homogeneity is a concern). Follow the Qualifier Flow Charts to see if reanalysis is necessary, or if result may be qualified. -If reanalysis is necessary for digests, rerun both the parent and the duplicate digestate. -For digestates, double-check that the correct weight information in the Calib/QC page is entered, then re-analyze. -After re-analysis, if the RPD is still poor there is likely a homogeneity issue. Run an AD (analytical duplicate) within the batch to fulfill QC requirements
Discrepancies between work order, bench sheet and physical samples.	Differences in #of samples or types of analysis. Unusual QC requirements	-General rule-Don't start until you know what exactly you are doing. Conflicts should be dealt with at the beginning of your analysis. -When in doubt ask, usually the project managers. They are the easiest and best way to find out what is truly going on.

17) Calculations:

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17.1 Methyl Mercury in Water

17.1.1 Only IBL is being used to correct the peak area values from the strip chart.

17.1.2 The average calibration factor (A) is calculated using the peak area values and known concentration of methyl mercury. The calibration points are first corrected by subtraction of the ICB. Then the individual calibration point response is divided by the expected concentration of methyl mercury. The average calibration factor is determined from all calibration points and used to convert sample response to concentration.

17.1.3 Average the results for the preparation blanks (PB), from the peak areas of at least three preparation blanks.

17.1.4 To calculate methyl mercury in waters (ng/L), use the following equations.

MeHg Initial Result (ng/L) = [[[[(Peak Area)-B]/A]*DS/E]-[[(PB)-B]/A]*DB/E]/DS

MeHg Final Reported Result (ng/L) = [[(MeHg Initial Result)*D*[Vf/Vi]

Where:

B is the peak area of the IBL.

A is the calculated average calibration factor (in units/(ng/L)).

Vf is the final prepared volume of the sample analyzed in mL.

Vi is the initial prepared volume of the sample analyzed in mL.

DS is the instrumental dilution of the sample compared to the volume of the calibration points.

DB is the instrumental dilution of the blanks compared to the volume of the calibration points.

PB is the average peak areas of the preparation blanks.

If the sample is not being prep blank corrected, the [[(PB)-B]/A]*DB/E term equals 0.

E is the empirically-derived efficiency factor

17.2 Methyl Mercury in Solids:

17.2.1 To calculate methyl mercury in a solid digestion or extraction (ng/g), use the following equations:

MeHg Initial Result (ng/L) = [[[[(Peak Area)-B]/A]*DS]-[[(PB)-B]/A]*DB]/DS

MeHg Final Result (ng/g) = [[(MeHg Initial Result)*D*[Vf/Vi]

Where:

B is the peak area of the IBL.

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A is the calculated average calibration factor (in units/(ng/L)).

Vf is the final prepared volume of the sample analyzed in mL.

Vi is the initial prepared mass of the sample analyzed in mg.

DS is the instrumental dilution of the sample compared to the volume of the calibration points.

DB is the instrumental dilution of the blanks compared to the volume of the calibration points.

PB is the average peak areas of the preparation blanks.

If the sample is not being prep blank corrected, the [[(PB)-B]/A]*DB term equals 0.

17.2.2 To calculate methyl mercury in a solid distillation (ng/g), use the following equations:

MeHg Initial Result (ng/L) = [[[[(Peak Area)-B]/A]*DS/E]-[[(PB)-B]/A]*DB/E]/DS

MeHg Final Result (ng/g) = [[(MeHg Initial Result)*D*[Vf/Vi]

Where:

B is the average peak area.

A is the calculated average calibration factor (in (ng/L)/units).

Vf is the final prepared volume of the sample analyzed in mL.

Vi is the initial prepared mass of the sample analyzed in mg.

DS is the instrumental dilution of the sample compared to the volume of the calibration points.

DB is the instrumental dilution of the blanks compared to the volume of the calibration points.

PB is the average peak areas of the preparation blanks.

If the sample is not being prep blank corrected, the [[(PB)-B]/A]*DB/E term equals 0.

E is the empirically-derived efficiency factor

18) Statistical Information/Method Performance:

18.1 Method Detections Limits (MDL) are determined during method development and then annually thereafter according to 40 CFR Part 136, Section B and CA-Q-S-006.

18.2 The Practical Quantitation Limit (PQL) is the reporting limit for this method and must be included as the lowest calibration point.

18.3 Using clean handling and reagents low in mercury, low level LOD and PQL levels are attainable.

18.4 Current MDLs, LODs, and PQLs can be found in the LIMS.

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18.5 The method detection limit (MDL) listed in Table 1 in method EPA 1630 and the quality control acceptance criteria listed in Table 2 in EPA 1630 were validated in four laboratories. In addition, the techniques in this method have been inter-compared with other techniques for low-level CH_3Hg determination in water in the International Mercury Speciation Inter-comparison Exercise (reference 15 in EPA 1630, this SOP 2.10).

18.6 Eurofins Seattle has been participating in inter-comparison studies when available, since there are no proficiency studies available for methyl mercury analysis.

19) Quality Assurance/Quality Control:

19.1 An analytical batch is defined as 20 or fewer client samples. QC samples such as: BLKs, BS/BSD, ICV, ICB, CCVs, CCBs, or matrix QC (MD, MS, or MSD) are excluded.

19.2 One CCV/CCB should be performed every 10 analytical runs. The method requirement is that a CCV/CCB pair must be analyzed every 12 hours.

19.3 One MS/MSD pair must be analyzed for every 10 samples. For a batch up to 20, two sets of MS/MSDs must be analyzed. MS/MSDs are spiked according to the work order instructions or the default spiking level. The true value of spikes will change if a smaller sample mass is digested.

19.3.1 For aqueous samples, the general MS/MSD spiking level is 0.050 ng of methyl mercury into 50 mL of sample (1.0 ng/L). Client samples can be spiked at higher or lower concentrations depending on historical data, specified by the Project Manager or Senior Analyst.

19.3.2 For soil/sediment samples, the default spiking level is 2.5 ng of methyl mercury into 0.5 g of sample (5.0 ng/g).

19.3.3 For tissue samples, the default spiking level is 20 ng of methyl mercury into 0.250 g of sample (40 ng/g).

19.4 A matrix duplicate (MD) or matrix triplicate (MT) may be prepared with each batch upon client request. MD and MT samples should be analyzed using the same sample aliquots as the ambient sample. The MSD may serve as the MD.

19.5 One matrix specific CRM or blank spike must be performed in duplicate with each batch (LCS/LCSD in LIMS).

19.5.1 Due to the lack of a CRM for methyl mercury in water, one BS/BSD must be analyzed per analytical batch. The spiking levels may vary depending upon the client, and will be performed during preparation. Refer to work order, project managers, senior analyst, or group leader for specific spiking levels. The default spike addition for BS/BSD is 0.050 ng of methyl mercury into 50mL of reagent water (1.0ng/L). The BS/BSD goes through the same sample preparation procedure as the samples.

19.6 Three preparation blanks must be performed with each batch.

19.7 At the end of an analytical run *must* conclude with an OPR/CCB.

19.8 Analysts are to verify QC sample results in "real-time" as they come off the instrument. This allows for correction of any analytical problems immediately.

19.9 Results that fall out of acceptable criteria range may be qualified using the flowcharts in EFQA-P-DR-SOP2801 (data review).

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19.10 In most cases, the acceptance criteria listed below must be met in order for a data set to be considered valid. Of particular importance to the client is Eurofins Seattle's position that a single non-compliant result on a QC sample does not automatically invalidate a data set. Data points initially noted on the analysis day's spreadsheet as invalid for known reasons may be discarded if a rerun is performed during the same analysis day.

19.11 Quality Control Limits for Determination of Methyl Hg

QC Item	Acceptance Criteria
Calibration Factor RSD	</=15%
All Calibration Standard Recoveries	65-135% recovery
ICV (0.5 ng/L secondary source)	69-131% recovery for waters 65-135% recovery tissues/soils/sediments
CCV (0.5 ng/L)	67-133% for waters 60-140% for tissues/soils/sediments
MD	No MD required
MS/MSD	65-135% recovery for waters 50-150% for tissues/soils/sediments RPD ≤ 35% (all matrices)
LCS/LCSD	65-135% recovery for waters 50-150% for tissues/soils/sediments RPD ≤ 35% (all matrices)
ICB (blank injected after ICV)	< LOQ (< ½LOQ for DoD samples)
CCB (blank injected after CCV)	< LOQ (< ½LOQ for DoD samples)
Preparation Blanks (see below for DoD requirements)	< LOQ (< ½LOQ for DoD samples)

19.12 For DoD samples, the method blank will be considered to be contaminated if:

19.12.1 The concentration of any target analyte in the blank exceeds 1/2 the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater);

19.12.2 The concentration of any common laboratory contaminant in the blank exceeds the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater); or

19.12.3 The blank result otherwise affects the samples results as per the test method requirements or the project-specific objectives.

19.12.3.1 If the method blank is contaminated as described above, then the laboratory shall reprocess affected samples in a subsequent preparation batch, except when sample results are below the LOD. If insufficient sample volume remains for reprocessing, the results shall be reported with appropriate data qualifiers.

19.13 Initial precision and recovery (IPR) – to establish the ability to generate acceptable precision and recovery, the analyst shall perform the following operations.

19.13.1 Analyze four replicates of at 0.5 ng/L.

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19.13.2 Using the results of the set of four analyses, compute the average percent recovery (X), and the standard deviation of the percent recovery (s) for CH3Hg.

19.13.3 If the average percent recovery is within 69-131% and the standard deviation is less than 31%, the IPR is acceptable. This IPR is equal to the IDOC that is required per TNI standards.

19.14 Manual Integrations. At times, manual integration is necessary to correct inappropriate automatic integrations. In order to document this, a chromatogram is first generated with the initial inappropriate integration. In the x-axis header, the analyst must type "DNR - <IntegrationReason> - <AnalystInitials> <DateOfManualIntegration>" filling in the integration reason tag from the list of reasons in the table below. After this, the integration is changed and the final chromatogram is generated. Both of these must be included in the final data package. Secondary reviewers are required to check the appropriateness of all manual integrations and are also responsible with ensuring compliance with the requirements stated in section for documentation of manual integrations for this method.

Integration Reason	Integration Reason Definition
PI	Peak Not Integrated
SI	Sample Matrix Interference
IN	Instrument Noise
II	Incomplete Integration
SP	Split Peak
WP	Wrong Peak
AP	Assign Peak
BS	Baseline Smoothing
SH	Shouldering
PT	Peak Tail

20) Corrective Action

20.1 The quality control data gathered throughout the analytical day provides an indication of overall data quality. Therefore, corrective action is required if quality assurance measures are outside of acceptable limits. First, a careful re-examination of the data entry and calculations is performed to assure that there are no numerical errors. The project manager is informed of the data issue. The analyst will decide what corrective action, including reruns, is warranted. The analyst is responsible for creating re-extracts in LIMS and alerting the Group Leader that reanalysis is necessary. The Quality Assurance Officer has the final say in what corrective action is to be performed.

20.2 If insufficient sample volume remains to repeat analysis for samples analyzed after the last acceptable CCV/OPR, provide a narrative explanation in the work order (in the MMO section) and/or on the data review checklist. Estimated values must be flagged in LIMS and in the report to the client.

20.3 The above corrective actions apply only to events which have unknown causes. If the analyst is aware of the cause, no corrective action is necessary other than reanalyzing the sample and documenting appropriately.

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20.4 If an MD/MT fails, and the sample concentration is greater than 5 times the PQL and the difference is less than 1 times the ambient sample and the duplicate should be reanalyzed for confirmation, if possible. The undigested sample should be inspected for heterogeneity, and a note made in the work order (MMO) and/or data review checklist. A poor RPD may be qualified according to the Data Qualifier Flowcharts included in *EFGS-P-DR-SOP2801* (data review).

20.5 Continuing Calibration Verification (CCV): if a recovery falls outside acceptance criteria, re-calibrate the instrument and reanalyze all affected samples since the last acceptable CCV or immediately analyze two additional CCVs. If both CCVs are within acceptance criteria, the samples may be reported without reanalysis and the analysis of the next bracket may continue beginning with a CCB.

20.5.1 If either of the two CCVs fails, the analysis must be terminated, the problem resolved, the instrument re-calibrated and then all of the affected samples since the last acceptable CCV reanalyzed.

21) List of Attachments

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Appendix A

Determination of Ethyl Mercury

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1) Purpose

1.1 To outline the standard, reagent and procedural differences needed in EFAFS-T-AFS-SOP2808 to adapt the procedure to the analysis of water samples for ethyl mercury. Due to the high concentration of mercury in these samples, the samples are not distilled prior to analysis. The minimum dilution on these samples is 500-fold.

2) Apparatus and Equipment:

2.1 Program ETF for Tekran 2700: For ethyl mercury analysis, the program ETF used for this analysis is "psample15" supplied by the instrument manufacturer.

3.) Reagents and Standards:

3.1 Propylating Agent: Sodium Tetrapropylborate (Made with the same process as the ethylating agent).

3.1.1 Vendor is Ryan Scientific Inc

3.2 Primary Standard: Ethyl Hg (5.0585 µg/g of C_2H_5Hg) or 4.4184 µg/g as Hg

3.2.1 Vendor is Applied Isotope Technologies, Inc (PN-30017.A1)

3.3 Calibration Standards: Two different level of standards are used for the calibration

3.3.1 High level standard is a 2500x of the parent source (Cal3 is 20µL in 50mL, Cal4 is 50µL in 50mL and Cal5 is 200µL in 50mL)

3.3.2 Low Level standard is a 50x of the High level Standard (Cal1 is 200µL in 50mL and Cal2 is 400µL in 50mL)

4) Procedure

4.1 Follow EFAFS-T-AFS-SOP2808 with the following modifications

4.1.1 Propylating agent is used instead of ethylating agent. When it's necessary to switch from one agent to another, a reverse purging of the sample line and probe is recommended to ensure the previous agent is removed from the system.

4.1.2 Calibration of the instrument is described in section 3.3.

4.1.3 There is no secondary standard for ethyl mercury, so the primary is used for CCVs. Ethyl mercury is present in the MHg-ICV standard, so CCVs for each analyte are analyzed separately.

4.1.4 A retention time study was performed on three different calibrations on three different days. The retention time window calculated for ethyl mercury from this study is 199 to 266

seconds. This retention window needs to be applied to the ethyl mercury analysis.

4.1.5 MS/MSDs can be spiked with MHg and EHg standards.

5) Calculations

5.1 The standard MHg analysis calculations apply to these samples. Since the samples are not distilled, an efficiency factor is not applied.

5.2 The recovery limits established for MHg are applied to this analysis.

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EFGS-P-DR-SOP2801 Data Review and Validation and Monthly Logbook Reviews
EFGS-P-SP-SOP2811 Sample Preservation and Splitting for Trace/Specialty Metals
EFGS-Q-QD-SOP2710 Class 1 Weight Calibration, Balance Verification, Calibration & Maintenance
EFGS-Q-QD-SOP41510 Volumetric Verification and Pipette and Dispenser Operation & Maintenance
EFGS-Q-QM-QM5805 Quality Assurance Manual
EFGS-S-CS-SOP2794 Ultra-Clean Aqueous Sample Collection
EFGS-S-HS-QP12066.0004 Chemical Hygiene Plan
EFGS-S-HS-SOP2991 Waste Disposal Procedures for Client Sample Waste
EFGS-S-IT-WI7061 Eurofins Frontier Global Sciences - Instrument and Instrument Software Inventory
EFGS-S-SB-SOP5139 Cleaning of Sampling Equipment and Bottles for Trace Metals Analysis
EFGS-S-T-SOP2806 Preparation of Tenax- and Carbo-Traps for Methyl- and Dimethyl Mercury Analysis
EFGS-T-AFS-SOP2797 Distillation of Aqueous Samples for Methyl Mercury Analysis
EFGS-T-AFS-SOP2986 KOH/Methanol Digestion of Tissues for Methyl Mercury Analysis
EFGS-T-AFS-SOP5134 Preparation of Sediments by Acidic Potassium Bromated Extraction into Methylene Chloride for the Determination of Methyl Mercury
EFGS-T-TM-SOP2839 Stock and Prepared Standards

End of document

Version history

Version	Approval	Revision information	
9	05.JAN.2023		
10	07.MAR.2024		
10.1	21.JUN.2024		

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DOCUMENT IS NOT CONTROLLED WHEN PRINTED

1) Revision Log:
2) Reference:
3) Cross Reference:
4) Purpose:
5) Scope:
6) Basic Principles:
7) Reference Modifications:
8) Definitions:
9) Interferences:
10) Safety Precautions, Pollution Prevention and Waste Handling:
11) Personnel Training and Qualifications:
12) Sample Collection, Preservation, and Handling:
13) Apparatus and Equipment:
14) Reagents and Standards:
15) Calibration:
16) Procedure:
17) Calculations:
18) Statistical Information/Method Performance:
19) Quality Assurance/Quality Control:
20) Corrective Action
21) List of Attachments

1) Revision Log:

Revision: 8	**Effective Date:** This version	
Section	**Justification**	**Changes**
Throughout	Required	Updated laboratory name to Eurofins Seattle
8.38	Required	Removed high calibration verifications
13.1	Required	Updated computer OS requirements
14.3.1	Required	Removed nitric acid tip rinse, not used
14.4.3.2	Required	Updated criteria to 0.2 ng/L
15	Required	Updated calibration concentrations
15.1.1	Required	Clarified IBL criteria requirements
15.2	Required	Added recovery criteria for all calibration points
15.3	Required	Removed high calibration verifications
16.3.1	Required	Removed specific concentration requirement for IPR/IDOC
16.4.1	Required	Removed specific concentration requirement for IPR/IDOC
16.5.1	Required	Updated to require IPR/IDOC for air matrix
16.5	Required	Removed KCl trap information
16.5.5.2	Required	Removed MS/MSD reference (n/a to air)
18.2	Required	Updated PQL definition
18.3	Required	Updated limit storage information to LIMS
Table 1	Required	Updated QC limits

Revision: 7.2D	**Effective Date:** 05/11/2023	
Section	**Justification**	**Changes**
16.3.2	Required	Corrected preservation time for aqueous samples

2) Reference:

2.1 EPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, 2002.

2.2 Method 1669, "Method for Sampling Ambient Water for Determination of Metals at EPA Ambient Criteria Levels," U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Engineering and Analysis Division (4303), 401 M Street SW, Washington, DC 20460, April 1995 with January 1996 revisions.

2.3 Bloom, N.S.; Ultra-Clean Sample Handling, Environmental Lab 1995, March/April, 20.

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2.4 Bloom, N.S.; Horvat M., and Watras C.J. Results of the International Mercury Speciation Intercomparison Exercise. Wat. Air Soil Pollut. 1995, 80, 1257.

2.5 Bloom, N.S.; Crecelius, E.A. Determination of Mercury in Seawater at Sub-nanogram per Liter Levels.Mar.Chem.1983, 14, 49.

2.6 Bloom, N.S.; Crecelius, E.A. Distribution of Silver, Lead, Mercury, Copper, and Cadmium in Central Puget Sound Sediments Mar. Chem 1987, 21, 377-390.

2.7 Bloom, N.S.; Fitzgerald, W.F. Determination of Volatile Mercury Species at the Picogram Level by Low-Temperature Gas Chromatography with Cold-Vapor Atomic Fluorescence Detection. Anal. Chem. Acta. 1988, 208, 151.

2.8 Cossa, D.; Couran, P. An International Intercomparison Exercise for Total Mercury in Seawater. App.Organomet. Chem.1990, 4, 49.

2.9 Fitzgerald, W.F.; Gill, G.A. Sub-Nanogram Determination of Mercury by Two-Stage Gold Amalgamation and Gas Phase Detection Applied to Atmospheric Analysis. Anal. Chem. 1979, 15, 1714.

2.10 Gill, G.A.; Fitzgerald, W.F. Mercury Sampling of Open Ocean Waters at the Picogram Level Deep Sea Res.1985, 32, 287.

2.11 Chapter NR 149, Lab Certification and Registration, Wisconsin Administrative Code.

2.12 TNI Environmental Laboratory Sector, Vol 1, Management and Technical Requirements, ELV1-2016.

2.13 Department of Defense / Department of Energy Consolidated Quality Systems Manual for Environmental Laboratories, prepared by DoD Environmental Data Quality Workgroup (EDQW) and DOE Consolidate Audit Program (DOECAP) Data Quality Workgroup (DOE-DQW), Version 5.3, May 2019.

3) Cross Reference:

Document	Document Title
EFGS-Q-QM-QM5805	QA Manual
CA-Q-S-006	Detection and Quantitation Limits
EFGS-Q-QD-SOP2710	Class 1 Weight Calibration, Balance Verification, Calibration & Maintenance
EFGS-Q-QD-SOP41510	Volumetric Verification and Pipette and Dispenser Operation & Maintenance
EFGS-S-SB-SOP5139	Cleaning of Sampling Equipment and Bottles
EFGS-S-CS-SOP2794	Ultra-Clean Aqueous Sample Collection
EFGS-T-TM-SOP2839	Stock and Prepared Standards
EFGS-T-AFS-SOP2985	Digestion of Gas/Air Samples Collected on FSTM Traps
EFGS-T-AFS-SOP2800	Digestion of KCL Traps for Total Mercury
EFGS-T-AFS-SOP2795	Digestion of Tissues for Total Mercury Analysis Using Nitric and Sulfuric Acids (70:30)
EFGS-P-DR-SOP2801	Data Review and Validation and Monthly Logbooks Reviews
EFGS-T-TM-SOP2837	Total Recoverable Metals Digestion for Animal or Plant Tissues
EFGS-T-AFS-SOP2807	Preparation of Solid Samples for Total Mercury Analysis by Modified Cold Aqua-Regia Digestion
EFGS-S-HS-SOP2991	Waste Disposal Procedures for Client Sample Waste
EFGS-T-TM-SOP2821	HF/HNO3/HCl Bomb Digestion of Sediments, Soils, Rocks, and Bayer Process Solids and Slurries for Mercury, followed by Repeated HNO3 Evaporation

4) Purpose:

4.1 This standard operating procedure (SOP) describes a method for the determination of total mercury (Hg) in a wide range of matrices including, but not limited to, aqueous, biological, and geological media. Total mercury is measured by Flow Injection Atomic Fluorescence Spectrometry and is calculated on a concentration (ppt) basis by comparing the instrument response of samples to the instrument response of standards.

4.2 This SOP is designed to ensure that reproducible traceable procedures are followed in the standardization of the total mercury analyzers and in the analysis of samples for total mercury, as well as to establish the limits wherein data will be considered acceptable.

5) Scope:

5.1 This method is designed for the determination of mercury in the typical range of 0.5-80 ng/L (ppt). Samples with mercury concentrations outside the designated calibration range can only be analyzed at a dilution.

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5.2 This SOP describes a method of the determination of mercury species in aqueous and solid matrices (biological tissue, plant tissue, nutraceutical, etc.).

6) Basic Principles:

6.1 Total mercury analyses are split into two categories: waters and solids. For analysis of aqueous samples, a dilution (up to 1x) of oxidized sample is added to a 50mL vial. If less than 30mL of sample is used, the sample is diluted to a final volume of at least 30mL with 1% BrCl. For solids, a appropriate dilution (based on specific preparation method) is made of the digested sample by pipetting into a 50mL vial and diluting it to 50mL with 1% BrCl. In the case of waters and solids, the final volume is neutralized with 50 uL of 25% hydroxylamine-hydrochloride (NH2OH-HCl). Approximately 20mL of sample is aspirated by an auto sampler (Please refer to Figure 1 for a detailed system flow diagram of the Tekran 2600 analysis system). This sample is then mixed with 3% stannous chloride ($SnCl_2$) which reduces Hg^{2+} ions to Hg^0 before introduced to the top of a phase separator.

6.2 As sample travels down the phase separator, Hg^0 is liberated by a counter-current flow of ultra-pure argon (or nitrogen). This mercury then travels through a soda-lime acid vapor trap and a switching valve (V2) and amalgamates onto the fixed gold quartz trap. Following primary amalgamation, V2 is triggered which switches on the flow of pure argon through the sample trap. At the same time, the gold quartz trap is heated and mercury is released into the pure argon gas stream. The mercury passes through a second switching valve (V1) and amalgamates onto a pure gold "analytical trap." The analytical trap is then heated and V1 is switched, which introduces the mercury into the AFS detector. All event timing and peak integration is carried out via a PC running TekMDS-2 software running the EPA 1631 "Sample" event timing file (ETF).

(NOTE: This method may also be run using 15ml vials and selecting the appropriate ETF with in the TekMDS-2 software. Sample must fill the vial up to the 15ml mark. All other procedures, reagent concentrations, and dilutions should be kept the same.)

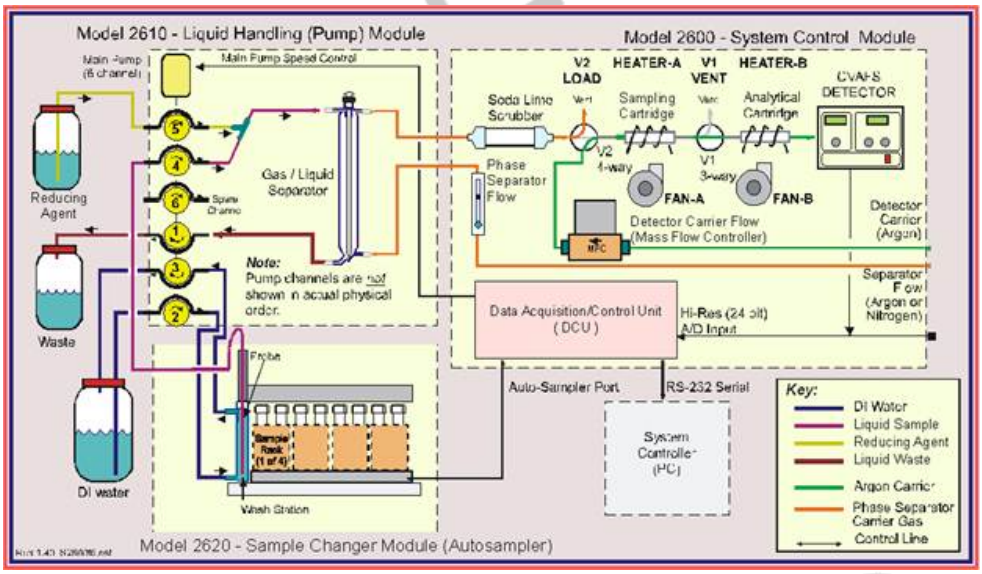


Figure 1 - Tekran 2600 Flow Diagram

7) Reference Modifications:

7.1 There were no significant modifications made to this method.

8) Definitions:

8.1 Analytical Duplicate (AD): A representative sample (that yielded a result within the calibration curve) is analyzed a second time during the analytical run. The second analysis should be at the same aliquot as the original.

8.2 Analytical Run – The continuous analysis of one or more batches during the same 12 hour-shift. Each analytical day requires 3 IBLs (instrument blank levels), a minimum five-point calibration curve, ICV, and CCV/CCB every ten sample injections following the initial calibration. An analytical day must conclude with a CCV/CCB. An analytical run may conclude with a CCVH and CCB.

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8.3 Analytical Spike and Analytical Spike Duplicate (AS/ASD): A representative sample is selected and spiked, with a dilution of the primary source, during the analytical run, at a target concentration of 1-5X the ambient concentration of the sample. These QC samples are used to indicate sample matrix effects on the analyte of interest. Non-detectable samples are spiked at 5x the MRL/PQL.

8.4 Batch: 20 client samples or less grouped for preparation. See Quality Assurance Section for batch requirements.

8.5 Calibration Standards (CAL) – a series of non-zero standards that will be used to calibrate the instrument, made from a primary source stock standard. Three calibration blanks plus at least five different concentrations are required, beginning with one at PQL concentration or lower.

8.6 Certified Reference Material (CRM) – a standard of known composition that is certified by a recognized authority and representing a sample matrix. It is used to verify the accuracy of a method.

8.7 Continuing Calibration Verification (CCV): A dilution of the OPR standard resulting in an instrumental concentration of 5.0ng/L. This standard is analyzed every 10 analyses after the ICV, and determines whether the instrument is maintaining calibration.

8.8 Continuing Demonstration of Capability (CDOC): Acceptable performance on a PT sample or a new IDOC or a set of four (4) consecutive blank spike or laboratory control sample aliquots [prepared according to a method by an analyst or technician that are analyzed by the same or different analyst or technician according to a method] that meet established and documented criteria for precision and accuracy to assess the ongoing proficiency of the analysts or technicians.

8.9 Control Limit (CL) – the limit of the range of acceptability for the quality control samples

8.10 Equipment Blank (EB): Reagent water processed through the sampling devices and placed in a sample container prior to using the equipment to collect samples and used to demonstrate that the sampling equipment is free from contamination.

8.11 Field Blanks (FB): A sample of reagent water placed in a sample container in the field and used to demonstrate that samples have not been contaminated by sample collection or transport activities. EPA-1631E recommends the analysis of at least one field blank per 10 samples collected at the same site at the same time. It is recommended to analyze these blanks before analyzing the client samples in the batch.

8.12 Initial Calibration Verification (ICV) –A dilution of the OPR standard resulting in an instrumental concentration of 5.0 ng/L. This standard is run immediately following the calibration curve and verifies instrument calibration.

8.13 Initial Precision and Recovery (IPR) – A dilution or digestion of a secondary source resulting in an instrumental concentration of 5.0 ng/L mercury.

8.14 Instrument Blank Level and Continuing Calibration Blank (IBL and CCB) for evaluation of instrument drift, sensitivity and contamination. At least 3 IBLs must be analyzed before the first calibration standard, and the CCBs every 10 samples immediately after CCVs.

8.15 Initial Demonstration of Capability (IDOC): A set of four (4) blank spike or laboratory control sample aliquots prepared according to a method by an analyst or technician at the concentration specified by the group manager (or if unspecified, to a concentration of one (1) to four (4) times the limit of quantitation) that are analyzed by the same or a different analyst or technician according to a method. The mean and standard deviation of the four results are calculated and compared to established and documented criteria for precision and accuracy to assess the initial proficiency of the analysts or technicians before they independently process client samples.

8.16 Laboratory Control Sample (LCS and LCSD) or Quality Control Sample (QCS): A sample (and duplicate) containing a known concentration of mercury that is used to monitor complete method performance. The preferred LCS is a matrix matched Certified Reference Material (CRM), but a blank spike meets the requirement also. In LIMS, the LCS is always referred to as a Blank Spike (BS), whether it is matrix matched or not.

8.17 Limit of Detection (LOD) – The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%. The LOD shall be at least 2 times but no greater than 4 times the DL for multiple analyte methods or 2 times but no greater than 3 times the DL for single analyte methods.

8.18 Limit of Quantitation (LOQ) – equal to PQL (practical quantitation limit) or reporting limit (RL) and verified on a quarterly basis by spiking at or below the LOQ and showing a recovery within method specified control limits for laboratory control samples.

8.19 LIMS: Laboratory Information Management System. Computer software used for managing samples, standards, and other laboratory functions.

8.20 May: This action, activity, or procedural step is optional.

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8.21 May Not: This action, activity, or procedural step is prohibited.

8.22 Matrix Spike (MS) and Matrix Spike Duplicate (MSD): A representative sample is selected and spiked with a dilution of the primary source at a known concentration. The MS and MSD are run through the entire analytical process just as the samples are. These QC samples will indicate sample matrix effects on the analyte of interest.

8.23 Method Blank (MB)=): For waters, reagent water that is prepared and analyzed in a manner identical to that of samples. For digested solids, preparations blanks consist of the same reagents used to digest the samples, in the same volume or proportion and are carried through the complete sample preparation and analytical procedure. Boiling chips are used as a blank matrix for solids. Preparation blanks are referred to as BLK in LIMS.

8.24 Method Detection Limit (MDL): A limit derived from 40 CFR, Part 136, Appendix B. This method produces a defined value that is the minimum concentration that can be measured and reported with a 99% confidence that the analyte concentration is greater than zero from a given matrix.

8.25 Method Duplicates/Method Triplicates (MD/MT): A second or third separate sample dilution, taken from the same source sample, prepared and analyzed in the laboratory separately.

8.26 Reagent water: 18 MΩ minimum, reagent water starting from a pre-purified (distilled, Reverse Osmosis, etc.) source.

8.27 Must: This action, activity, or procedural step is required.

8.28 Ongoing Precision and Recovery (OPR): A dilution of a secondary source resulting in an instrumental concentration of 5.0 ng/L mercury.

8.29 PM: Project Manager.

8.30 Primary Source: The stock standard used to make the calibration standard. Procedural Method: A method where standards and samples are run through the analytical procedure exactly the same. By NELAC definition, this SOP is a procedural method.

8.31 Secondary Source: The stock standard used to make the OPR standard

8.32 Shall: This action, activity, or procedure is required.

8.33 Should: This action, activity, or procedure is suggested, but not required.

8.34 Stock Standard Solution (SSS) – a standard of analyte that is purchased from a certified source for the preparation of working standards.

8.35 Total mercury: As defined by this method, all bromine monochloride-oxidizable mercury forms and species found in aqueous solutions. This includes, but is not limited to, Hg2+, Hg0, strongly organo-complexed Hg(II) compounds, adsorbed particulate Hg(P), and several tested covalently bound organomercurials (i.e. CH3HgCl, (CH3)2Hg, and C6H5HgOOCCH3). The recovery of mercury bound within microbial cells may require additional preparation steps (i.e. UV oxidation, or oven digestion).

8.36 Travel or Trip Blank (TB): A sample of reagent water placed in a sample container in the laboratory and used to demonstrate that samples have not been contaminated by transport activities.

8.37 Wash Station Blank (WSB) – a "blank" that is aspirated from the instrument rinse station (0.5% BrCl). At least three WSBs are used at the beginning of analysis to assess overall cleanliness of the system/reagents. WSBs may also be used mid-run to flush the system after running a high level sample, or check the mercury levels in the wash station.

9) Interferences:

9.1 Due to high levels of acid and halogens (i.e. bromide) in digested solids, it is recommended that these digestates be analyzed at a 10x dilution or higher.

9.2 Improperly adjusted pump tubing can cause the phase separator to fill with sample. In extreme situations, the overflow can back up into instrument causing damage to the traps and switching valves. Care must be taken to insure the pump tubing tension is properly set. DO NOT OVER TIGHTEN**.**

9.3 The minimum digestate dilution that should be analyzed if HF acid, FSTM material, or coal is present in significant concentrations is a 50x dilution. Samples prepared according to *EFGS-T-TM-SOP2821* are diluted before analysis, therefore a 10x dilution is the minimum.

9.4 Water vapor has the potential to create recovery interferences. To prevent interference from water, ensure that soda-lime pre-traps and gold traps remain dry.

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9.5 The presence of high concentrations of silver and/or gold can cause SnCl2 to precipitate out of solution and adhere to the tubing and/or phase separator walls. High concentrations of these metals can sometimes be found in the matrix spike samples from the digestion sets that are shared with the trace metals group.

9.6 Analysis of samples containing high concentrations of strong acids (>2%) can cause passivation of the sample trap and lead to low bias/recoveries. When analyzing samples containing >2% strong acid (at the instrument), the analyst should verify that passivation is not an issue by running a Hg spike into MQ water containing a similar concentration of acid. If the spike recovers low (<90%) passivation may be an issue and the sample may need to be diluted.

9.7 If elemental Hg is spilled in the facility, contamination can occur to all uncapped reagents and those not stored in gas-impermeable containers. See Appendix 1 for instructions on analysis post elemental Hg spill.

10) Safety Precautions, Pollution Prevention and Waste Handling:

10.1 Personnel will don appropriate laboratory attire according to the Chemical Hygiene Plan (*EFGS-S-HS-12066*). This includes, but is not limited to, laboratory coat, eye protection and protective gloves.

10.2 The toxicity or carcinogenicity of reagents used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Chemists should refer to the SDS (Safety Data Sheets) located at https://msdsmanagement.msdsonline.com/company/5c1df5b3-747d-4789-8104-42457dc3a3e5/ for each chemical they are working with.

> **10.2.1** Note: Use particular caution when preparing and using BrCl, as it releases extremely irritating, corrosive fumes similar in effect to free chlorine. Always handle this reagent in an approved fume hood.

10.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease-causative agents. Eurofins Seattle will reimburse the expense of Hepatitis A and B immunizations for any laboratory staff member who desires this protection.

10.4 Hydrochloric acid: Very hazardous in case of skin contact (corrosive, irritant, permeator), of eye contact (irritant, corrosive), of ingestion. Slightly hazardous in case of inhalation (lung sensitizer). Non-corrosive for lungs. Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. Severe over-exposure can result in death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering. For more information see SDS.

10.5 See Eurofins Seattle Chemical Hygiene Plan (CHP) for general information regarding employee safety, waste management, and pollution prevention.

10.6 Pollution prevention information can be found in the current Eurofins Seattle Chemical Hygiene Plan (CHP), which details and tracks various waste streams and disposal procedures.

10.7 All laboratory waste is accumulated, managed, and disposed of in accordance with all federal, state, and local laws and regulations. Any waste generated by this procedure should be disposed of according to SOP *EFGS-S-HS-SOP2991* "Waste Disposal Procedure for Client Sample Waste," which provides instruction on dealing with laboratory and client waste

11) Personnel Training and Qualifications:

11.1 An analyst must perform an initial demonstration of capability (IDOC) that includes four replicates of a secondary source before being qualified to analyze samples without supervision. Continuing DOC will be maintained and monitored via performance on CRMs and other QC samples, as well as obtaining acceptable results on proficiency testing exercises.

11.2 The analyst/laboratory technician must have read this SOP and other relevant SOPs and have the training documented on the applicable form(s). The analysis may be questioned on SOP by supervisor(s) and/or trainers.

11.3 Training is documented by the employee and supervisor, and is kept on file in the QA Office. The employee must read, understand, and by signing the training document, agree to perform the procedures as stated in all Standard Operating Procedures (SOPs) related to this method.

11.4 All employees must read the Quality Manual (*EFGS-Q-QM-QM5805*) and complete annual Ethics training.

11.5 All training documents including IDOCs, CDOCs, Initial QA orientation, and Ethics training are stored by the Quality Assurance Manager in the employees training file for ten years after the employee is no longer working for Eurofins Seattle.

11.6 Chemical Safety Training, Compressed Gas Training, Chemical Hygiene Plan documentation, and Shipping of Hazardous

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goods, are stored by the Health and Safety Officer for ten years after the employee is no longer working for Eurofins Seattle.

12) Sample Collection, Preservation, and Handling:

12.1 Aqueous samples are collected in rigorously cleaned fluoropolymer (e.g. Teflon) bottles and caps (as described in *EFGS-S-SB-SOP5139* "Cleaning of Sampling Equipment and Bottles for Mercury Analysis"). Certified clean glass bottles with fluoropolymer lids may be used if mercury is the only analyte of interest.

12.1.1 Aqueous samples are preserved upon receipt with 0.2N BrCl that has tested low in mercury. Samples are typically preserved to 2% BrCl v/v, but may require further oxidation due to high levels of organic matter or mercury. Refer to *EFGS-T-AFS-SOP2992* "Mercury in Water by Oxidation".

12.2 Solid samples may be collected in glass, high density polyethylene, or fluoropolymer jars.

12.2.1 Solid samples are preserved by freezing upon receipt.

12.3 Impinger solutions preserved with nitric acid or containing potassium permangante (this category includes proficiency testing samples) need to be preserved with BrCl to insure the complete oxidation of organic species.

12.4 All samples should be collected utilizing clean techniques, so as not to cross-contaminate samples with mercury. See *EFGS-S-CS-SOP2794* "Ultra Clean Aqueous Sample Collection" and EPA Method 1669 for aqueous sample techniques.

13) Apparatus and Equipment:

13.1 LIMS – TALS; Computer – Windows 10 or higher

13.2 Tekran TekMDS-2 software (see instrument software log *EFGS-S-IT-WI17061*).

13.3 Tekran Model 2600 System Control Module. This module contains dual stage pre-concentration/desorption units, a high resolution analogue to digital converter, and a high sensitivity AFS Detector (IDL<1pg).

13.4 Tekran Model 2610 Pump Unit. This module contains a precision 6 channel peristaltic pump with optical speed feedback. Speed may be varied manually or under computer control. The pump head has three four-roller channels to providing high pumping rates for wash station circulation and waste removal, and three eight-roller channels to providing slower/low pulse delivery of $SnCl_2$ and sample (one extra channel).

13.5 Model 2620 Auto-Sampler – a specially modified Gilson Model 223 auto-sampler, includes reticulating wash station and allows for automatic sample handling with the 2600 analysis system.

13.6 50mL polypropylene vials with screw caps, manufactured by CPI International (Item No: 4092-450MP). Equivalent pre-cleaned and/or tested vials, graduated (class A) to 50mL may also be used.

13.7 Three-stop tubing, various inner diameters of Marprene for $SnCl_2$ (1.02mm), for wash station fill (2.38mm), wash station drain (2.79mm), and phase separator drain (2.79mm) Three-stop silicone tubing (2.05mm) is used for sample feed.

13.8 Teflon Fittings and FEP tubing (1/16" ID) of various sizes and lengths. This tubing is used for the sample probe, $SnCl_2$, phase separator, wash station, drain lines, and between gold traps.

13.9 Soda-Lime trap. This is a 14cm long, 1.1cm diameter glass tube filled with reagent grade, non-indicating 8-14 mesh soda-lime ($Ca(OH)_2$+NaOH) aggregates packed between portions of silanized glass wool. This trap is purged of mercury using a ultra-pure argon gas stream for at least 20 minutes. After purging, the trap is installed and the system rinsed with 3% $SnCl_2$ reductant and 0.5% BrCl wash station for approximately 5 minutes.

13.10 Phase separator – manufactured by Tekran. The phase separator facilitates laminar fluid flow of liquid sample over a frosted rod counter-current to a stream of ultra-pure argon gas at approximately 400mL/min.

13.11 Gold-Coated Quartz Sand Trap ("sample trap") – manufactured by Tekran or made in house, heated from 0% to 100%, 8 Amp maximum.

13.12 Pure Gold Bead Trap ("analytical trap") – manufactured by Tekran, heated from 0% to 100%, 8 Amp maximum.

13.13 Pipettes: Calibrated variable pipettes with a range of 5 µL – 10 mL. These are used to make solutions and sample dilutions. Pipettes are to be calibrated weekly according to SOP *EFGS-Q-QD-SOP41510* or daily if DOD samples are analyzed.

13.14 Analytical Balance – capable of accurately weighing to the nearest 0.1mg, and able to tare at least one gram. The analytical balances are verified for accuracy on a daily basis according to *EFGS-Q-QD-SOP2710*, "Balance Verification, Calibration and Maintenance.

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14) Reagents and Standards:

14.1 Reagent Water: 18-MΩ ultra pure deionized water starting from a pre-purified (distilled, reverse osmosis, etc.) source is used. To remove any remaining trace metals and organics, an activated carbon cartridge is placed between the final ion exchange bed and the 0.2-µm filter. Reagent water used in the mercury lab is checked weekly for total mercury concentrations, and must test below 0.25ng/L.

14.2 Concentrated (36-38% weight basis) Trace-Metal Grade Hydrochloric Acid (HCl): This HCl is lot-tested (analyzed like a water sample) at an 100x dilution. This reagent must test below 0.25ng/L. Do not prep blank correct.

14.3 Concentrated (69%-70% weight basis) Trace-Metal Grade Nitric Acid (HNO_3): Trace metal purified reagent-grade nitric acid is pre-analyzed and lot sequestered. Several brands (Baker, Fisher, Omnitrace) have been found to have lots with acceptably low levels of trace metals. This reagent should be from a lot number that has been previously tested to be low for the analytes of interest. This reagent shall be entered into LIMS and the expiration date is set to the same as the manufacturer's expiration date.

14.4 0.2N Bromine Monochloride (BrCl):

14.4.1 2.5 L of concentrated trace-metal grade HCl (14.2) is added to a 2.5 L glass jug. To this, 27 g of KBr is added and the bottle is inverted. The solution then sits overnight allowing for the KBr to be dissolved .

14.4.2 38 g of $KBrO_3$ (certified to be low in Hg) is slowly added to the acid. When all of the $KBrO_3$ is added, the solution should go from yellow to red to orange. **CAUTION: This process generates copious amounts of free halogens (Cl_2, Br_2, BrCl) which are released from the bottle. Add the $KBrO_3$ SLOWLY in a properly operating fume hood.**

14.4.3 Loosely cap the bottle and allow to sit for 1 hour in a fume hood before tightening. Once tightly capped, invert bottle to make sure all of the solids goes into solution.

14.4.3.1 The expiration time for this reagent is set by default to six months in LIMS. As there is no suggested holding time in EPA method 1631E, the holding time can be extended as long as the primary reagents have not expired. The mercury concentration of the BrCl is monitored through the preparation of water preparation blanks. Bottles of 0.2N BrCl suspected to be contaminated should never be used for analysis.

14.4.3.2 All 0.2N BrCl bottles should be tested before use. To test, add 50 µL of 25% hydroxylamine-HCl to a 50 mL vial. Add 1.0 mL of the 0.2N BrCl to this same vial and dilute to 50mL with reagent water. This reagent must test below 0.2 ng/L (do not prep blank correct). Analyze at least one replicate per bottle.

14.4.3.3 0.5% BrCl Rinse Solution: 30mL concentrated low-level mercury BrCl into 6,000mL of reagent water.

14.4.3.4 1.0% BrCl Solution: 10 mL of 0.2N BrCl brought to 1,000 mL final volume with reagent water.

14.4.3.5 2.0% BrCl Solution: 20 mL of 0.2N BrCl brought to 1,000 mL final volume with reagent water.

14.5 50% Hydroxylamine-HCl: Dissolve 500g of NH_2OH-HCl in reagent water and bring the volume up to 1L. Shake vigorously to ensure all added salt goes into solution. This solution may be purified by adding of 1mL of 50% $SnCl_2$ solution (14.6) and purging overnight at approximately 500 mL/min with ultra-pure argon. The working reagent is a 25% solution that is made by adding one part reagent water to one part 50% hydroxylamine hydrochloride. This reagent must test below 0.25ng/L.

14.5.1 To test the 50% Hydroxylamine-HCl solution, add 0.1 mL of the 50% reagent to a 50mL vial, dilute to 50mL with reagent water, and analyze like a normal water sample. This reagent must test below 0.25 ng/L (do not prep blank correct). Analyze one replicate per bottle.

14.6 50% Stannous Chloride ($SnCl_2$): Add 1000 g $SnCl_2 \bullet 2H_20$ to a thoroughly-rinsed 2.5 L glass bottle (a funnel made with weighing paper is extremely helpful here). Using a pump dispenser, add 600 mL concentrated trace-metal grade HCl (14.2) to this bottle. Bring the solution to a final volume of 2 L and mix thoroughly and carefully. This solution should be purged overnight with ultra-pure argon to remove all traces of mercury. Store this solution in a fume hood and keep it tightly capped. The working reagent is a 3% solution that is made by diluting 150mL of 50% $SnCl_2$ to 2.5L with reagent water.

14.6.1 To test the Stannous Chloride (SnCl2), add 0.3 mL of the 50% reagent to a 50 mL vial, dilute to 50 mL with reagent water, and analyze like a normal water sample. This reagent must test below 0.25 ng/L (do not prep blank correct). Analyze one replicate per bottle.

14.6.2 The expiration time for this reagent by default is set to six months in LIMS. As there is no suggested holding time in EPA method 1631E, the holding time can be extended as long as the primary reagent has not expired.

14.7 Total Mercury Stock and Prepared Standards: Alternate volumes of any of these standards may be prepared so long as the ratio of the components is kept constant.

14.7.1 See SOP *EFGS-T-TM-SOP2839* for information regarding the receipt, documentation, preparation, and storage of purchased and prepared standards.

14.7.2 Total Mercury Stock Standard Solution (Stock): Certified mercury standard purchased from High Purity Standards (1000 µg/mL (1 000 000 ng/mL) primary source) or Absolute Standards (100 µg/mL (100 000 ng/mL) secondary source), or any equivalent standard. If standards of differing concentrations are purchased, it is the analyst's responsibility to ensure the recipes for reagents 14.7.3 through 14.7.8 are altered appropriately.

14.7.3 100,000 ng/mL Spiking Standard: If made from the Primary Stock Standard (High Purity, or equivalent vendor). Dilute 10 mL of the stock standard to 100 mL RO water containing 2 % BrCl in a volumetric flask. (Can also be made by preserving Secondary Stock Standard to 2% BrCl). Expiration date is currently set at 6 months or when the stock standard expires, whichever is shorter.

14.7.4 10,000 ng/mL Spiking Standard: If made from the Primary Stock Standard (High Purity, or equivalent vendor). Dilute 1.0 mL of the stock standard to 100 mL RO water containing 2 % BrCl in a volumetric flask. If made from Secondary Stock Standard dilute 10mL of stock standard to 100mL with RO water containing 2% BrCl. Expiration date is currently set at 6 months or when the stock standard expires, whichever is shorter**.**

14.7.5 1,000 ng/mL Spiking Standard: If made from the Primary Stock Standard. Dilute 0.250 mL of the stock standard to 250 mL RO water containing 2 % BrCl. If made from Secondary Stock Standard, dilute 2.5mL of stock standard to 250mL with RO water containing 2% BrCl. Expiration date is currently set at 6 months or when the stock standard expires, whichever is shorter**.**

14.7.6 100 ng/mL Spiking Standard: Made from a stock standard or dilution of a stock standard with a concentration of 100,000 ng/mL. Dilute 0.100 mL of the 100,000 ng/mL dilution to 100 mL RO water containing 2 % BrCl. Expiration date is currently set at 3 months or when the stock standard expires, whichever is shorter.

14.7.7 Calibration Standard (10 ng/mL): Must be made from a dilution of the Primary Stock Standard. Typically made by diluting 0.5mL of a 10,000 ng/mL Primary Spiking Standard to 500 mL of RO water containing 2 % BrCl. Transfer to one 1000 mL glass or Teflon bottle. The calibration standard is considered stable for three months or until the stock standard expires.

14.7.8 OPR Standard (10 ng/mL): Must be made from a dilution of a Secondary Spiking Standard. Typically made by diluting 1.0mL of a 1000ng/mL Secondary Spiking standard to 100mL with RO water containing 2% BrCl.

14.7.9 Initial Calibration Verification (ICV): This solution is made daily. To make 500 mL of ICV solution, add 500 µL of 25% hydroxylamine-HCl solution to approximately 100 mL of water in a 500 mL volumetric flask. Add 10 mL of 0.2N BrCl and swirl to reduce the BrCl to dilute acid. Finally, add 250 µL of OPR standard (14.7.8) and carefully bring to a final volume of 500 mL. The (nominal) mercury concentration of this solution should be 5.0 ng/L. The expiration date of this solution should match that of the OPR standard used to prepare it.

14.7.10 Continuing Calibration Verification (CCV): The ICV solution (14.7.9) is to be used for all CCV injections throughout an analytical run.

14.7.11 Argon Grade 4.7 or better (ultra high-purity grade) – argon that has been further purified by the removal of mercury using a gold trap that is located in line between the gas output and the analyzer gas input.

15) Calibration:

15.1 The calibration sequence consists of three IBLs followed by a minimum 5-point calibration curve using the calibration factors method. Usual concentrations are 0.5ppt, 1.0ppt, 5.0ppt, 20.0ppt, and 80.0ppt, analyzed from lowest to highest. The calibration must include a point at 0.5 ppt or lower. Additionally, the analyst may include points above 80.0 ppt so long as they can demonstrate carryover is not present for any matrix that will be analyzed. After the chosen calibration standards are analyzed, an ICV/OPR (5.0 ppt) is injected and the calibration is assessed before any client samples are run.

15.1.1 Three IBLs are prepared by adding 50mL of 2.0% BrCl to a sample vial. The uncorrected response of these IBLs must be under 0.5ppt (with a standard deviation less than 0.1 ppt) once the calibration factor has been determined. If it is higher, then analysis should be halted and the cause determined (reagent contamination is a common cause).

15.1.2 Calibration standards at or above 5.0 ppt should be created as stock solutions in a manner similar to how the ICV solution is created in 14.7.9. To create solutions at concentrations lower than 5.0 ppt, it is recommended that the analyst dilute their most concentrated stock solution. Below is an example of how a set of calibration standards (0.5 ppt, 1.0 ppt, 5.0 ppt, 20.0 ppt, 80.0 ppt) might be created:

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- 0.5 ppt: Created as a dilution of the 20.0 ppt stock solution. Add 50 µL of 25% hydroxylamine-HCl to a 50 mL vial. To this, add 1250 µL of 20.0 ppt stock solution and bring to 50 mL final volume using 2.0% BrCl.

- 1.0 ppt: Created as a dilution of the 80.0 ppt stock solution. Add 50 µL of 25% hydroxylamine-HCl to a 50 mL vial. To this, add 625 µL of 80.0 ppt stock solution and bring to 50 mL final volume using 2.0% BrCl.

- 5.0 ppt: Created as a stock solution. To make 500 mL of 5.0 ppt stock solution, add 500 µL of 25% hydroxylamine-HCl solution to approximately 100 mL of water in a 500 mL volumetric flask. Add 10 mL of 0.2N BrCl and swirl to reduce the BrCl to dilute acid. Finally, add 250 µL of 10.0 ng/mL primary standard (14.7.7) and carefully bring to a final volume of 500 mL.

- 20.0 ppt: Created as a stock solution. To make 500 mL of 20.0 ppt stock solution, add 500 µL of 25% hydroxylamine-HCl solution to approximately 100 mL of water in a 500 mL volumetric flask. Add 10 mL of 0.2N BrCl and swirl to reduce the BrCl to dilute acid. Finally, add 1000 µL of 10.0 ng/mL primary standard (14.7.7) and carefully bring to a final volume of 500 mL.

- 80.0 ppt: Created as a stock solution. To make 500 mL of 80.0 ppt stock solution, add 500 µL of 25% hydroxylamine-HCl solution to approximately 100 mL of water in a 500 mL volumetric flask. Add 10 mL of 0.2N BrCl and swirl to reduce the BrCl to dilute acid. Finally, add 4000 µL of 10.0 ng/mL primary standard (14.7.7) and carefully bring to a final volume of 500 mL.

15.2 A initial calibration is considered acceptable if and only if (1) the corrected response factor relative standard deviation is less than or equal to 15%, (2) the recovery of all calibration standards is between 75% to 125%, and (3) the IBL concentration meets the criteria stated in 15.1.1.

15.3 Once the instrument is calibrated with an acceptable calibration (see section 15.2) and the ICV/OPR has been analyzed and passes, the instrument is considered operational. The sample concentrations must fall within the range of the calibration standards or be diluted and reanalyzed.

15.4 The calibration of this system and calculation of sample results are performed using units of concentration (ppt or ng/L).

16) Procedure:

16.1 Pre-analysis and Organization:

16.1.1 Prior to analyzing samples it is imperative to reference LIMS for all project specific information, such as QC requirements, suggested dilutions, project manager information, and specifics regarding spike levels.

16.1.2 The analyst should then locate samples and check the work order in LIMS for notes about specific project requirements.

16.1.3 The analyst should compare the sample IDs to the work order and see that the samples are accounted for, and notify the project manager of any discrepancies in analysis required, sample identification, etc.

16.1.4 All mercury analyses receive a unique dataset identifier and LIMS assigned sequence number. The dataset ID is comprised of the instrument type and number, the date and the calibration number for that day. The format is as follows: THg26001-130216-1, where "THg "refers to a total mercury analysis; "26001" refers to Tekran 2600 instrument number 1; 130216 refers to the date (February 16, 2013 in the YYMMDD format); and "1" refers to the first calibration of the day. The sequence number is assigned by LIMS when the data gets imported into LIMS. The alpha-numeric code is based on the following format: 3B02001, where the 3 refers to the year (2013), the "B" is the month (A= January, B=February… L=December), "02" is the day of the month (February 2nd) and the final 3 digits is the nth sequence created on that particular year/month/day combination.

16.1.5 In general the analyst should organize their samples in the order listed on the bench sheet. The first samples analyzed should be the preparation blanks, then the LCS if analyzing solid samples, followed by actual samples. If possible, run total and dissolved samples side by side to facilitate verification that total concentration is greater than dissolved concentration. See QA section.

16.2 Instrument Start Up:

16.2.1 If necessary, prepare the soda-lime trap. The soda-lime trap should be changed at least every three analytical days.

16.2.2 Start the TekMDS software and check to make sure the computer is communicating with the instrument and the autosampler. Load a new work sheet and begin to enter the sample IDs into the run. Take care to insure that the appropriate autosampler position and dilution are entered correctly into the worksheet.

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16.2.3 Empty the waste carboy in accordance with EFHS-S-HS-SOP2991 "Waste Dumping Procedure for Client Sample Waste.

16.2.4 Fill rinse basin with a fresh solution of 0.5% BrCl and refill 3% $SnCl_2$ container.

16.2.5 Check tubing for wear and re-index or replace as needed. Clamp all tubing/cassettes onto pump head and adjust tension. Do not over-tighten.

16.2.5.1 Insure that there are no kinks in reagent or waste lines.

16.2.6 Turn the pump on to "local" and check flow of all reagents, including flow through the sample probe from the wash station and flow of SnCl2 into phase separator. Adjust tension on tubing, if necessary. Be sure that the waste line is flowing well and waste does not back-up into the phase separator! This can often be prevented by loosening the tension on the tubing for both the phase separator drain and the wash station drain. Allow it to run with reagents for 20 minutes.

16.2.7 All analytical runs should begin with at least two "clean" cycle to "blank" the gold traps, followed by three wash station blanks (WSB) to assure that the system is free of mercury.

16.2.8 Set pump back to "remote" to start the run.

16.2.9 Note: It is important to check the flow, reagent levels, and waste carboy level throughout the analytical run. If a reagent is low in volume, it can be refilled mid-run. Similarly, the waste carboy should be emptied mid-run, if necessary. The SnCl2 and sample flow (tension on tubing) cannot be changed mid-run as it may affect instrument response. For this reason, it is important to verify proper sample/reagent flow prior to beginning analysis.

16.3 Batching and Analyzing Aqueous Samples:

16.3.1 All analysts will show Initial Precision and Recovery (IPR) by analyzing four secondary spikes. The spikes need to recover between 79-121% with an RSD < 21%.

16.3.2 All aqueous samples should be preserved with BrCl at least 24 hours prior to analysis. In the event a sample requires further oxidation prior to analysis, additional BrCl is added and the sample is not analyzed for at least 24 additional hours. In special cases where rush turn-around-time is required and an oxidation period of less than 24 hours may be used, the analyst should consult a supervisor for approval. The supervisor must be able to confirm (based on past experience) that the particular matrix type is completely oxidized before analysis.

16.3.3 It is recommended that all known field, equipment, and trip blanks should be analyzed before any other sample types.

16.3.4 For all samples, ensure an appropriate dilution is selected prior to vialing (refer to LIMS, historical data, minimum dilutions, etc.).

16.3.5 When preparing dilutions, use calibrated pipettes to dispense the aliquots into the 50mL vials. Dilute the sample to a final volume of 50mL with 2% BrCl and neutralize with 50µL of 25% NH2OH-HCl. The sample should turn from a yellowish color to a clear/cloudy solution, depending on the matrix. Be sure to note any sample dilutions onto the bench sheet for cross referencing during peer review. Note that the analyst may choose a smaller final volume (no less than 30 mL) so long as the ratio of sample to 25% NH2OH-HCl is preserved (e.g. 40 µL of 25% NH2OH-HCl for a 40 mL final volume). Note that volumetric verification at each final volume must be performed for every lot of tube received.

16.3.6 If a 1x dilution of a water sample is possible, the sample first must be thoroughly homogenized. Then, 50 mL of sample is poured directly into 50mL vial already containing 50 µL of 25% NH_2OH-HCl. The analyst may choose to use a smaller volume of sample (no less than 30 mL) so long as the ratio of sample to 25% NH_2OH-HCl is preserved (e.g. add 30 mL of sample to 30 µL of 25% NH_2OH-HCl).

16.3.7 Load sample vials into the auto sampler. Verify that the correct vial is in the proper position relative to the analysis worksheet entry in TekMDS software for that sample.

16.3.8 For each sample, the sample ID and a dilution is entered into the TekMDS software. For water samples preserved to greater than 2% BrCl, a comment should be made stating the preservation percentage (and an appropriate preservation blank should be analyzed). Unless otherwise stated (e.g., all WI DNR samples, PRASA), all aqueous samples should be PB corrected. Note that all prep blank correction takes place after analysis in an Excel spreadsheet, not in the TekMDS software.

16.3.9 The analyst should continue preparing and adding samples to the run in the same fashion to maximize efficiency. Positions on the autosampler can be used more than one time throughout the analysis run by removing a previously analyzed sample vial and replacing it with a new sample.

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16.4 Analysis of Digested Solids:

16.4.1 All analysts will show Initial Precision and Recovery (IPR) by analyzing four secondary spikes. The spikes need to recover between 75-125% with an RSD < 20% for solid and tissue preparations.

16.4.2 With this method it is possible to determine the concentration of total mercury in solid samples following proper digestion. The following highlight the majority of total mercury prep techniques for solids and their matrix specific SOPs.

16.4.2.1 For tissues, refer to *EFGS-T-AFS-SOP2795* "Digestion of Tissues for Total Mercury Analysis Using Nitric and Sulfuric Acids (70:30)" for the nitric acid/sulfuric acid digestion and *EFGS-T-TM-SOP2837* EFTM-T-TM-SOP2837 "Total Metals Digestion for Animal or Plant Tissues" for the concentrated nitric acid digest.

16.4.2.2 For soils/sediments, refer to *EFGS-T-AFS-SOP2807* "Preparation of Solid Samples for Total Mercury Analysis by Modified Cold Aqua-Regia Digestion" for the cold aqua regia digestion, *EFGS-T-AFS-SOP2795* for the nitric acid/sulfuric acid digestion, and *EFGS-T-TM-SOP2821* "HF/HNO3/HCl Bomb Digestion of Sediments, Soils, Rocks, and Bayer Process Solids and Slurries for Mercury, followed by Repeated HNO3 Evaporation" for the hydrofluoric acid/nitric acid bomb digestion.

16.4.2.3 For coal and ash, refer to *EFGS-T-AFS-SOP2807* Preparation of Solid Samples for Total Mercury Analysis by Modified Cold Aqua-Regia Digestion for the cold aqua regia digestion. For FSTM, refer to *EFGS-T-AFS-SOP2985* "Mercury Digest for Gas/Air Samples Collected on KCl/Quartz or KCl/Lime trap" for the digestion of traps.

16.4.3 After the instrument calibration sequence, preparation blanks, digested CRM(s), and LCS samples should be analyzed. For solid batches, the analyst should use the minimum dilution allowed for each preparation blank and diluting to 50mL with reagent water preserved to 2% BrCl. Analysts are to calculate the appropriate dilution for digested CRMs and LCS samples, ensuring that the sample concentration stays within the calibration curve. Analysts should also ensure that the recoveries for CRMs and LCS samples are within control limits before analyzing the associated batch samples.

16.4.4 Begin analyzing samples by the order of the digestion sheet, with the exception of the sample that has separate QC digested for MD/MS/MSD. It is appropriate to analyze this sample, and any associated QC, out of bench sheet order. The analyst should review any relevant project notes, historical data, or information given by client to the PM to help determine proper dilutions that will allow samples to recover within calibration curve. Note that the analyst may choose a smaller final volume (no less than 30 mL) so long as the ratio of sample to 25% NH2OH-HCl is preserved (e.g. 40 µL of 25% NH2OH-HCl for a 40 mL final volume). Note that volumetric verification at each final volume must be performed for every lot of tube received.

16.4.5 The procedure for analysis is similar to that of the calibration:

16.4.5.1 Selected digest samples are pipetted into a 50mL vial (one sample per vial) and diluted to 50mL with reagent water preserved to 2% BrCl. Ensure that appropriate dilutions are selected by consulting the minimum dilutions for the associated digests.

16.4.5.2 For each sample, the sample ID and dilution based on 50mL is entered into the TekMDS software. The dilution should also be noted on the digestion bench sheet for cross referencing in peer review. Unless otherwise stated, all solid samples should be PB corrected. Note: Prep blank correction takes place after analysis in the Excel spreadsheet, not in the TekMDS software.

16.4.5.3 After loading one set of samples, the analyst should begin preparing the next round of digested solid samples in the same fashion to maximize efficiency.

16.4.6 Quality Control Procedures for Digested Solid Samples:

16.4.6.1 Please refer to the appropriate SOP for each matrix's corresponding quality control samples. All quality control samples prepared for the batch should be run with its analysis unless stated otherwise by the project manager. Please see Table 1 for acceptance criteria.

16.4.6.2 Spiking standard LIMS ID and the amount used for the MS/MSD must be noted on the digestion bench sheet for cross referencing in peer review.

16.4.6.3 The analytical day must close with a CCV(OPR) /CCB.

16.5 Analysis of Fluegas Sorbent for Total Mercury (FSTM)/KCl Traps and Particulate Filter:

16.5.1 The IPR for air sample digestates (*EFGS-T-AFS-SOP2985*) has the same requirements as solid and tissue digestates.

16.5.2 With a few exceptions, FSTM traps and particulate filters are digested and analyzed as if they were solids.

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16.5.3 FSTM traps or particulate filters should be digested according to *EFGS-T-AFS-SOP2985* "Digestion for Gas/Air Samples Collected on Fluegas Sorbent for Total Mercury TM Traps."

16.5.4 The minimum dilution currently used for analysis should be 100x for FSTM diluted in 2% BrCl . Smaller dilution factors than these may be used at PM request, but is not recommended. To avoid any potential matrix interference it is recommended that the smallest reasonable aliquot sizes be used for this matrix. All blanks and low level/non-detect samples must be analyzed at the same dilution. Dilution should also be noted on the digestion bench sheet for cross referencing in peer review.

16.5.5 Quality Control Requirements for FSTM Traps and Particulate Filters:

16.5.5.1 Please refer to the appropriate SOP for each matrix's corresponding quality control samples. All quality control samples prepared for the batch should be run with its analysis unless stated otherwise by the project manager. Please see Table 1 for acceptance criteria.

16.6 End of analysis close-down procedure:

16.6.1 The gas flow to the phase separator automatically shuts off.

16.6.2 Move reagent lines to rinse carboy.

16.6.3 With pump set to "Local", rinse system for 5-minutes.

16.6.4 Release pump tubing for all but the "Sample" and "Waste" lines. Allow lines to drain.

16.6.5 Set pump to "Off".

16.6.6 Slowly release the "Sample" and" Waste" line. Carefully monitor the Wash station over the next 5 minutes, making sure it is not siphoning, or overflows.

16.6.7 Carryout all end of day cleaning and restocking tasks.

16.7 Analytical data is exported from the TekMDS software to an Excel file. The data is then copied and pasted into an Excel template that is LIMS compatible.

16.8 Tekran 2600 Mercury Analysis System Troubleshooting
The following is a summary of common troubleshooting techniques. This is not an all-inclusive list of what may be done to deal with analytical issues. Consultation with the group leader is preferred when performing these corrective actions. Analysts are encouraged not to rely on this guideline. Instead, this document should be used as a learning tool. Analysts should be actively striving to learn about troubleshooting as well as creative, productive ways of dealing with analytical issues.

16.8.1 ISSUE: No peaks at all

16.8.1.1 Ensure that the system is powered.

16.8.1.2 Make sure that the base line is approximately 0.1 V.

16.8.1.3 Make sure that you are running the right event table file (ETF).

16.8.1.4 Ensure that the carrier gas fitting is properly connected to the Argon source. (See System components, User guides, Section 2-3 for details).

16.8.1.5 Ensure that the phase separator gas fitting is properly connected to the Argon/Nitrogen source. (See System components, User guides, Section 2-3 for details)

16.8.1.6 Check operation of heater B. (Refer to Heater B Test)

16.8.1.7 Check operation of heater A. (Refer to Heater A Test)

16.8.1.8 Check that V2 is working properly. (Refer to V2 Test)

16.8.1.9 Check that V1 is switching properly. (Refer to V1 Tests)

16.8.2 ISSUE: Low sensitivity

16.8.2.1 Make sure that all "No peaks detected" samples are checked.

16.8.2.2 Check all connections to V2 and V1 and tighten all friction fittings up and downstream the Cartridges A and B.

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16.8.2.3 Make sure that you have freshly changed soda lime in the soda lime trap, and that it is from a good source.

16.8.2.4 Check and tighten all gas Teflon lines up and downstream of the soda lime trap and P/S.

16.8.2.5 Check the sample tubing following introduction of SnCl2 at the "Y" fitting for clogs. This line should also be the proper length.

16.8.2.6 Check that the frosted P/S rod is evenly wet. (Refer to P/S glass rod test).

16.8.2.7 Check that the tubing sizes in the main pump are correct. Also make sure that the tubing occlusion is set at the 12 o'clock position. Check the sample uptake (should be between 12 and 16 mL/min) and the SnCl2 uptake (should be between 3 and 5 mL/min).

16.8.2.8 Do not use old calibration standards to calibrate the system.

16.8.2.9 Make sure you are running fresh $SnCl_2$ solution.

16.8.2.10 Make sure that your stock Hg standard has not expired and is from a reliable source and that it is not compromised.

16.8.2.11 Check and tighten both sides of the ¼" straight Teflon union on the cuvette.

16.8.2.12 Check the cuvette (Refer to the System Component, User Guides Cuvette Removal and Cleaning, Section 4-3 and Cuvette cleaning procedure).

16.8.2.13 Check the lamp voltage. If the voltage is low, increase to required values (refer to System Component, User Guides Lamp voltage adjustment, Note 4-7).

16.8.2.14 Check both cartridges for failures

16.8.2.14.1 Check if Cartridge A is having problems. (Refer to Cartridge A test procedure).

16.8.2.14.2 Check if Cartridge B is having problems. (Refer to Cartridge B test procedure

16.8.3 ISSUE: HighBlanks

High blanks could be due to:
- Contamination in the system (liquid and/or gas lines)
- Water high in Hg
- Ambient Hg (in lab air)
- Poor quality of the reagents (KBr, $KBrO_3$, $SnCl_2$, Hydroxylamine, HCl etc).

16.8.3.1 Contamination in the system (liquid and/or gas lines), caused by:

16.8.3.1.1 System left without operating for an extended period of time (e.g. a month) and not shut down properly.

16.8.3.1.2 System not flushed and cleaned after running samples (especially high level samples). Note: Any sample over 200 ng/L requires a blank be ran after to check for carryover.

16.8.3.1.3 Following analysis of samples high in organics and not flushing properly after the run**.** Sudden contamination when an extremely high in Hg concentration sample is run through the system: From past experience this type of contamination is very dependent on the type of samples the analyst was running in the system more so than the exact concentration of Hg within the sample. There are cases when even after analysis of a very high sample (~1.0 ppb) the blanks will come back to normal very quickly. In other cases, effort will need to be made to lower the blanks. Basically the methods of cleaning are the same as those described below.

16.8.3.1.4 Not following normal and necessary maintenance procedures.

16.8.3.1.4.1 Addressing contamination in gas lines:

16.8.3.1.4.1.1 Bypass the P/S. (Refer to P/S bypassing procedure).

16.8.3.1.4.1.2 Continue by running some CLEAN cycles. If high peaks result, clean Cartridge B. (Refer to Cleaning the Cartridge B procedure).

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16.8.3.1.4.1.3 Continue running dry (Sample cycle). If at this point you still get high peak areas, clean Cartridge A (Refer to Cleaning the Cartridge A procedure).

16.8.3.1.3.1.5 Once again continue running dry. If you still get high peak areas, clean V2. (Refer to cleaning V2 procedure).

16.8.3.1.4.1.5 If high blank are still present, clean/replace the gas phase Teflon lines. (Refer to cleaning of the gas phase Teflon lines).

16.8.3.1.4.2 Addressing contamination in liquid lines:

16.8.3.1.4.2.1 Check/replace the silicone sample line.

16.8.3.1.4.2.2 Check/replace the sample/SnCl2 line to the P/S.

16.8.3.1.4.2.3 Check/clean the P/S. (Refer to Analytical Methods, Tekran Guide, Method 1631, section 5-1).

16.8.3.1.4.2.4 Clean system while running (Refer to clean while running procedure).

16.8.3.2 Poor water Quality

16.8.3.2.1 Refer to Analytical Methods, Tekran Guide, Method 1631, section 3-4

16.8.3.3 Poor quality of the reagents (KBr, KBrO3, SnCl2, Hydroxylamine, HCl etc)

16.8.3.3.1 Refer to Analytical Methods, Tekran Guide, Method 1631, section 3-4, 3-5.

16.8.4 ISSUE: Nonlinearity of the calibration curve

There are a few different types of non-linearity and factors causing them:

16.8.4.1 Cal. Factors which are very low for the low calibration points (0.5 and 1 ng/L) but better for the higher standards.

This is probably due to high Calblank values that cause lowest points of calibration to be affected during blank correction. Stop the run and go through the procedure for investigating High Blanks.

16.8.4.2 Cal. Factors are very erratic (no clear increasing or decreasing tendency

16.8.4.2.1 Dry spots on the glass rod of the P/S. (Refer to P/S glass rod test).

16.8.4.2.2 Check that you are running with fresh soda lime.

16.8.4.2.3 Check the heaters (Refer to Heater B test and Heater A test).

16.8.4.2.4 Check the silicone sample tubing for any twisting, pinching, or bubbles.

16.8.4.2.5 Check and tighten all liquid and gas phase connections.

16.8.4.2.6 Make sure your calibration standards are fresh and properly prepared.

16.8.4.3 Poor results for high calibration standards

16.8.4.3.1 Previously run samples with difficult matrixes or high acid vapor content could be a potential cause for this. Such matrixes, in very rare cases, could cause temporary passivation of Cartridge A, as well as temporarily poison the liquid lines. After running such difficult samples, the system needs a very thorough cleaning (see at the procedures High blanks). Running overnight in "dry" mode with the P/S flow between 50-100mL/min can also help.

16.8.4.4 Cal. Factors decrease moving up in concentration through the calibration curve

16.8.4.4.1 Improper preparation of the standards. Check and prepare fresh calibration standards.

16.8.4.4.2 Contaminated and expired soda lime. Change soda lime.

16.8.4.4.3 Loose P/S friction fittings: tighten them.

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16.8.4.4.4 Loose Soda lime trap fittings: tighten them.

16.8.4.4.5 Loose gold trap friction fittings: tighten/replace them.

16.8.4.4.6 Loose connection of the ¼" nuts on V1 and V2. Tighten them.

16.8.4.4.7 Loose connection on both sides of ¼" straight Teflon union to the cuvette. Tighten both sides.

16.8.4.4.8 Open and examine the cuvette (Refer to the System Component, User Guides Cuvette Removal and Cleaning, Section 4-3 and Cuvette cleaning procedure)

17) Calculations:

17.1 Average all instrument blanks (PHX) using the peak area values from the TekMDS software. Subtract the average (IB) from the peak area for each standard and sample.

17.2 Calculate the calibration factor (CFx) for mercury in each of the five standards using the mean instrument-blank-subtracted peak area and the following equation:

$$CF_x = PA_x - IB / C_x$$

Where:

17.2.1 PA_x=peak area for mercury in standard

17.2.2 IB=mean peak area for mercury in instrument blank

17.2.3 C_x=mass in standard analyzed (ng/L)

17.2.4 CF_x=Response Factor of each concentration

17.2.4.1 Average the five response factors to establish mean value: CF(Avg) (units/ng/L).

17.3 Sample results are then corrected for the average peak area values of at least three preparation blanks (PBs), unless otherwise requested or for samples originating from Wisconsin (Wisconsin does not permit method blank subtraction). This result is shown as the Initial Result on the Excel spreadsheet and in LIMS.

17.4 Total Mercury in Water:

$$Hg / Initial Result (ng/L) = ((((Peak Area - IB) / CF_{(Avg)}) \times D_s) - (PB_x \times D_b)) / D_s$$

$$THg Final Result (ng/L) = (THg / Initial Result) \times (D_s \times V_f) / V_i$$

Where:

17.4.1 $CF_{(avg)}$ = average response factor (in units/ng/L).

17.4.2 IB = average instrument blank peak area (in units)

17.4.3 V_f = final volume of sample analyzed in mL. The final volume should account for the added volume of BrCl needed for preservation. For instance, 100 mL of sample is preserved with 3% (v/v) BrCl. The final volume should be 103 mL.

17.4.4 V_i = initial volume of sample analyzed in mL prior to addition of BrCl.

17.4.5 D_s = final dilution factor of sample.

17.4.6 D_b = final dilution factor of corresponding blank results. All preparation blanks at the same preservation level must be analyzed at the same dilution.

17.4.7 PB_X= initial average (on instrument) of the preparation blanks in ng/L related to the preservation level of the samples (i.e., X=2 for a sample which is preserved at 2% BrCl), thus accounting for the extra contribution of mercury from the BrCl. Sample results are corrected for the average blank concentration of only the corresponding blanks preserved at the same BrCl preservation level. For example, if a sample is preserved at 2% and one PB was run at 2%, the sample is corrected using the results from that blank.

17.5 Total Mercury in Solids:

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$$THg / Initial Result (ng/L) = ((((Peak Area - IB) / CF_{(Avg)}) \times D_s) - (PB \times D_b)) / D_s$$

$$THg Final Result (ng/g) = (THg / Initial Result) \times (D_s \times V_f) / (m \times 1000)$$

Where:

17.5.1 $CF_{(avg)}$ = average response factor (in units/ng/L).

17.5.2 IB = average instrument blank peak area (in units)

17.5.3 V_f = final volume of the digested sample in mL.

17.5.4 m = initial mass of the digested sample in g.

17.5.5 D_s = final dilution factor of sample.

17.5.6 D_b = final dilution factor of corresponding blank results. All preparation blanks must be analyzed at the same dilution.

17.5.7 PB = initial average (on instrument) of the preparation blanks found in the digest in ng/L. The initial mass of the digestion blanks must be the default mass specific to the preparation.

18) Statistical Information/Method Performance:

18.1 Method Detections Limits (MDL) are determined during method development and then annually thereafter according to 40 CFR Part 136, Section B and and CA-Q-S-006.

18.2 The Practical Quantitation Limit (PQL) is the reporting limit for this method and is included as the lowest calibration point (2003 NELAC regulation 5.5.5.2.2.1.h.3). The PQL is referred to as the Reporting Limit (RL) in the LIMS.

18.3 Current LODs, LOQs, MDLs and PQLs are stored within the LIMS system.

19) Quality Assurance/Quality Control:

19.1 A minimum of three preparation blanks and one LCS/LCSD (preferably NIST 1641e), must be analyzed per preparation batch. The upper control limit for each preparation blank is equal to the LOQ (½ LOQ for DOD samples).

19.2 Initial Precision and Recovery test for water must be four spikes (at 5.0 ng/L) recovering between 79-121% with an RSD < 21%; the IPR for soil must be four spikes (at 8.0 ng/g) recovering between 75-125% with an RSD < 20%.

19.3 Matrix Spikes: One Matrix Spike/Matrix Spike Duplicate (MS/MSD) must be performed for every 10 samples. The recovery of the MS/MSD must be between 71%-125% recovery, and the Relative Percent Difference (RPD) below 24%. If an MS/MSD is out of control, the analyst should investigate to identify the source of the failure. The MS and MSD may be used as duplicates. Some failures may be qualified using QA Qualification Flow Charts (Appendix A).

19.3.1 For aqueous samples, the MS/MSD is spiked at 1 to 5 times the ambient concentration, with 0.25 ng being the minimum spiking level. Sample dilutions for the MS/MSD should be the same as the ambient sample dilution, if sufficient sample volume exists. NEVER ADD SPIKE DIRECTLY TO THE ORIGINAL SAMPLE CONTAINER UNLESS OTHERWISE INSTRUCTED.

19.4 Matrix Duplicates – Not required. A Matrix Duplicate (MD) or Matrix Triplicate (MT) may be analyzed for every batch of 20 samples upon client request. The MSD may serve as the MD if necessary. The Relative Percent Difference (RPD) and the Relative Standard Deviation (RSD) of duplicate samples must be less than 24%. Some failures may be qualified using QA Qualification Flow Charts.

19.4.1 For aqueous samples, analyze the parent, duplicate and triplicate at the same dilution.

19.5 Laboratory Control Standard (LCS) or Quality Control Sample (QCS): For every batch of samples, at least one LCS is processed and analyzed. The recovery of the LCS must be within 80-120% for the aqueous NIST 1641e. An LCS Duplicate (LCSD) should accompany the LCS.

19.5.1 For solid digestions, a Certified Reference Material (CRM) is the preferred LCS, but a blank spike may serve as an LCS if an appropriate CRM does not exist. The spiking level is based on client request, historical data, or a default of mid-curve. A duplicate blank spike must also be prepared as an LCSD. Recoveries need to be 75-125% with an RPD < 24%.

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19.5.2 For water batches, the LCS and LCSD are prepared by spiking 2% BrCl with an appropriate amount of primary calibration standard to a concentration of 5.0 ppt.

19.6 Ongoing Precision and Recovery (OPR): An OPR must be analyzed at the beginning and end of each analytical batch, or at the end of each 12-hour shift. The recovery of the OPR must be within 77-123% to be considered in control.

19.7 All calibration standards must be traceable to the original standard source. The calibration curve must be established at the beginning of the analytical run. It must include at least five different concentrations, with the lowest concentration equal to the PQL. The average response factor of each calibration standard is used to calculate the sample values. The RSD of the response factors must be less than 15% of the mean or the calibration fails.

19.8 ICV control limit is 79-121%, while the CCV control limit is 77-123%. The CCV is analyzed every 10 sample injections and at the end of an analytical run. CCBs are always analyzed after the CCVs.

19.9 Field Blanks: To be compliant with EPA 1631, clients must submit a field blank for each set of samples (samples collected from the same site at the same time, to a maximum of 10 samples).

19.9.1 If no field blanks are submitted by the client, their data will be flagged with "FB-1631." "Required equipment/field/filter blank not submitted by the client. The sample has been analyzed according to 1631E, but does not meet 1631E criteria."

19.10 Method or Preparation Blanks (BLK): Method blanks are used to demonstrate that the analytical system is free from contamination that could otherwise compromise sample results. Method blanks are prepared and analyzed using sample containers, labware, reagents, and analytical procedures identical to those used to prepare and analyze the samples.

19.10.1 A minimum of three method blanks per analytical batch are required.

19.10.1.1 For solid digests, these blanks are created by using trace-metal grade boiling chips or blank FSTM material in lieu of sample and taking it through the digestion process.

19.10.1.1 For aqueous samples, these three blanks are simply 2% BrCl neutralized with 50 µL of NH_2OH-HCl (identical to IBLs). If samples are preserved to higher than 2% BrCl, then a single blank at that BrCl percentage must be added to the batch (that sample's blank correction should come from this higher percentage blank).

19.10.2 If analyzed preparation blanks are higher than the LOQ associated with the preparation method (or ½ LOQ for DOD samples or 2.2 times the LOD for WI-DNR samples), then it is necessary to carefully assess the results.

19.10.2.1 If the blanks for water batches are outside of control limits, then the system is deemed out of control. These blanks may be rerun to confirm this, but if they confirm then analysis should be halted and the system investigated.

19.10.2.1.1 Our current reporting limits for water samples are based off 1% BrCl preservation. These reporting limits should be used for our current 2% preserved samples. However, in the case that a sample is preserved to 5% or higher, the reporting limits should be multiplied by the preservation percentage.

19.10.2.1 For blanks associated with solid digestion batches, the system is not necessarily out of control if a preparation blank comes back above the LOQ (watch the CCBs to assess whether or not the system blank level is in control as well). If sample results are 10x higher than the blank result, then the data can be qualified. Otherwise, the samples associated with the high blank must be re-digested.

19.11 Instrument Blanks (IBL): A minimum of three instrument blanks must be analyzed with each analytical batch (before the first calibration standard). To analyze an instrument blank, analyze a sample of reagent water preserved to 2% BrCl.

19.11.1 If the instrument blank is found to contain more than 0.50 ng/L (or the standard deviation of the three blanks is greater than 0.10 ng/L), the system is out of control. The problem must be investigated and remedied before proceeding, and any samples run must be reanalyzed.

19.11.1.1 The result for all instrument blanks must be ≤ 0.50ng/L with a standard deviation of 0.10 ng/L.

19.12 Initial Calibration Blanks (ICBs) and Continuing Calibration Blanks (CCBs): These blanks are identical to IBLs (2% BrCl neutralized with NH_2OH-HCl) and are used to assess the blank level of the system throughout the analytical run. To report data without qualification, these must all be below the LOQ for the associated preparation method.

19.12.1 For DOD samples to be reported without qualification, the ICB and all CCBs must be below ½ the LOQ for the preparation method.

19.12.2 For WI-DNR samples to be reported without qualification, the ICB and CCBs must be below 2.2 times the LOD for the preparation method.

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19.13 The analytical day must close with a CCV/OPR/CCB.

19.14 Since the method is done in real-time, it is EFGS' position that a single non-compliant QC sample result does not automatically invalidate a data set. All data points that can be explained and rerun with a passing result can be qualified. If the source of error cannot be corrected for a QC standard that day, none of the data can be validated. In the event that the system becomes out of control during the analysis day, all results bracketed between valid QC data points shall still be considered valid (CCV, OPR, CCB, etc).

19.15 The Control Limits are established from EPA 1631E.

19.16 Carryover: In 2020 a carryover study was completed monitoring Hg levels up to five times the top calibration point (200 ng/L). No carryover was detected during this study. Any sample ran with a concentration of Hg over 200 ng/L requires a blank be ran directly after to ensure there is no carryover. Additional samples may only be ran after the blank shows a concentration below the LOQ.

20) Corrective Action

20.1 The data is reviewed as in the QC section (or matrix specific QC section) for all parameters that pass specific requirements. If the data does not meet QC requirements for waters, it is reanalyzed for confirmation; if the failing MD/MS/MSD results confirm, another sample is used for the batch. For all digestions, it is qualified or submitted for reruns. Data may be qualified (based on scientific peer review) by the Group Supervisor, Project Manager, Lab Manager, or QA Officer.

> **20.1.1** Continuing Calibration Verification (CCV): If a recovery falls outside acceptance criteria, recalibrate the instrument and reanalyze all affected samples since the last acceptable CCV or immediately analyze two additional CCVs. If both CCVs are within acceptance criteria, the samples may be reported without reanalysis and the analysis of the next bracket may continue beginning with a CCB.
>
> > **20.1.1.1** If either of the two CCVs fails, the analysis must be terminated, the problem resolved, the instrument recalibrated and then all of the affected samples since the last acceptable CCV reanalyzed.

20.2 Control Chart data is generated through LIMS to monitor the performance of the CCV, LCS, MS, and MSD. This is done by the QA department.

20.3 Due to the real-time nature of the CVAFS method, failures must be investigated as they happen. If the source of the problem can be identified, and corrected, the samples may be rerun. If source of problem cannot be isolated, see the Senior Analyst, Group Supervisor, or Laboratory Manager for instructions.

20.4 The Senior Analyst, Group Supervisor, Laboratory Manager, or QA Officer must be informed if QC fails. It is also advisable to always alert the Project Managers.

21) List of Attachments

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Appendix 1: Hg Spill 3-Prep Contingency Plan
Table 1: QC Requirements for Total Mercury
Table 2: Troubleshooting Flow Chart

Appendix 1: Hg Spill 3-Prep Contingency Plan

Elemental Hg is sometimes used to remove sulfur post solvent extraction. In the case of a spill please follow the instructions below before analyzing.

On first attempt at analysis post spill, rinse or replace containers for working solutions and reagents. Prepare new working solutions from existing parent reagents. Avoid using CPI centrifuge tubes for reagent storage as contamination from the atmosphere has been found to occur in even capped tubes.

Attempt a calibration under normal conditions to test necessity of contingency. If the recoveries and/or blanks are high, proceed to prepare samples three at a time.

Start the calibration with a clean and washstations as normal. When washstations stabilize (two comparable results in a row) prepare the three IBLs and load immediately. Wait until the end of the second IBL to prepare the next three vials (CAL 1-3). Tubes can be labeled ahead of time, but do not pour BrCl until the instrument is finishing up the second IBL. Proceed through the rest of the calibration in this fashion, prepping the next three samples/QC for injection after the second injection of the previous three and loading immediately onto the instrument. If the IBLs and/or other blanks have results around or above the MRL, consider restricting analysis to samples likely to be qualifiable with regards to failing blanks. If the calibration continues to fail, remake reagents and parent reagents until source of contamination has been cleared.

Do not prepare and cap samples more than three in advance. The tubes can be contaminated through the caps, even when contained in the hood. Similarly, avoid making working reagents until they need to be replaced in order to minimize potential exposure. Run the instrument with only sealable reagent containers.

Continue analyzing one calibration under normal preparation conditions. If the calibration, including the ICB, is within control, expand preparation to one bracket at a time. Prep test blanks with increasing amounts of time prior to injection to determine further extensions to the amount which can be safely loaded onto the instrument without risk of significant contamination.

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Table 1: QC Requirements for Total Mercury

QC Parameter	Acceptance Criteria
Initial Calibration Verification (ICV)	79-121% Recovery
Continuing Calibration Verification (CCV)	77-123% Recovery
Ongoing Precision and Recovery (OPR)	77-123% Recovery
Initial Calibration Blank (ICB)/ Continuing Calibration Blank (CCB)	ICB and CCB ≤ 0.50ng/L (0.25 for DOD/DOE)
Laboratory Control Standard (LCS) or Quality Control Standard (QCS)	75-125% Recovery RSD ≤ 24%
Certified Reference Material	75-125% Recovery RPD ≤ 24%
Calibration Curve RSD (Referred to as "Corr. RSD CF" in Excel spreadsheet).	RSD of Calibration Response Factor ≤ 15%
Lowest Calibration Point	75-125%
Matrix Duplicate (MD) and Analytical Duplicate (AD)	≤ 24% RPD
Matrix Spike and Matrix Spike Duplicate (MS/MSD) ; Analytical Spike (AS) and Analytical Spike Duplicate (ASD)	71-125% Recovery ≤ 24% RPD

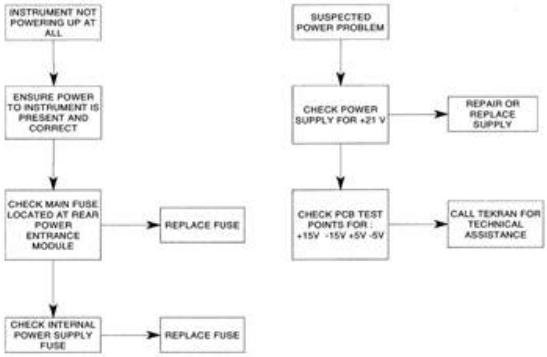
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Table 2: Troubleshooting Flow Chart

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NOTES: 1) Most problems with low responses can be traced to chemical/physical problems with auxiliary equipment.

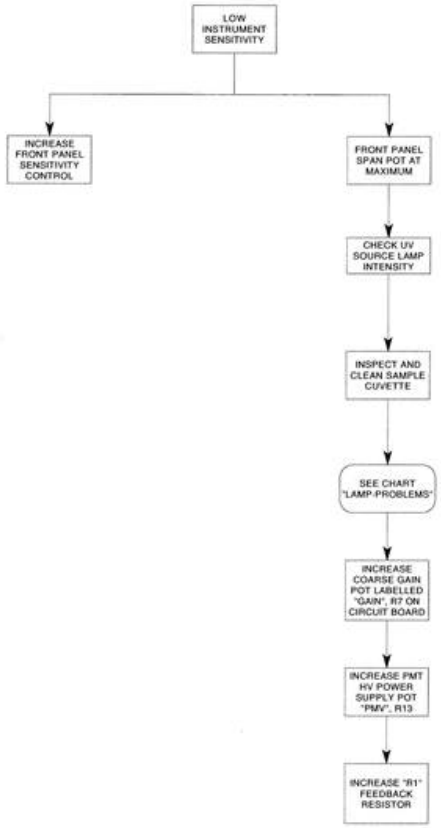
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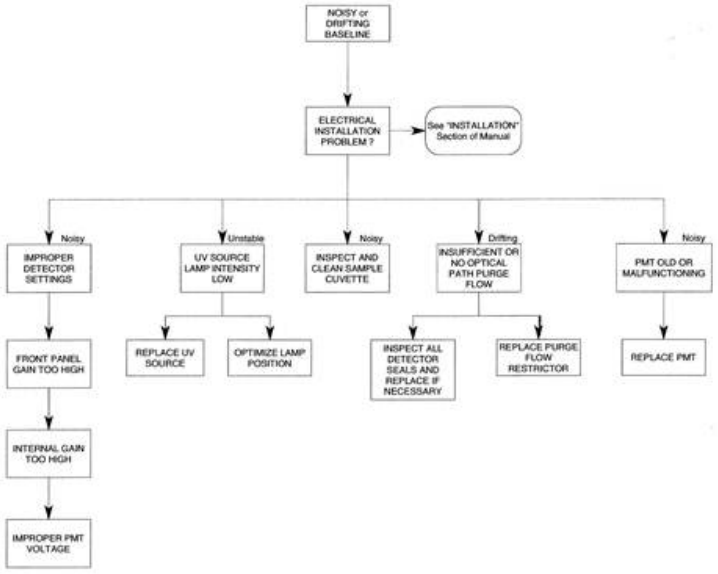
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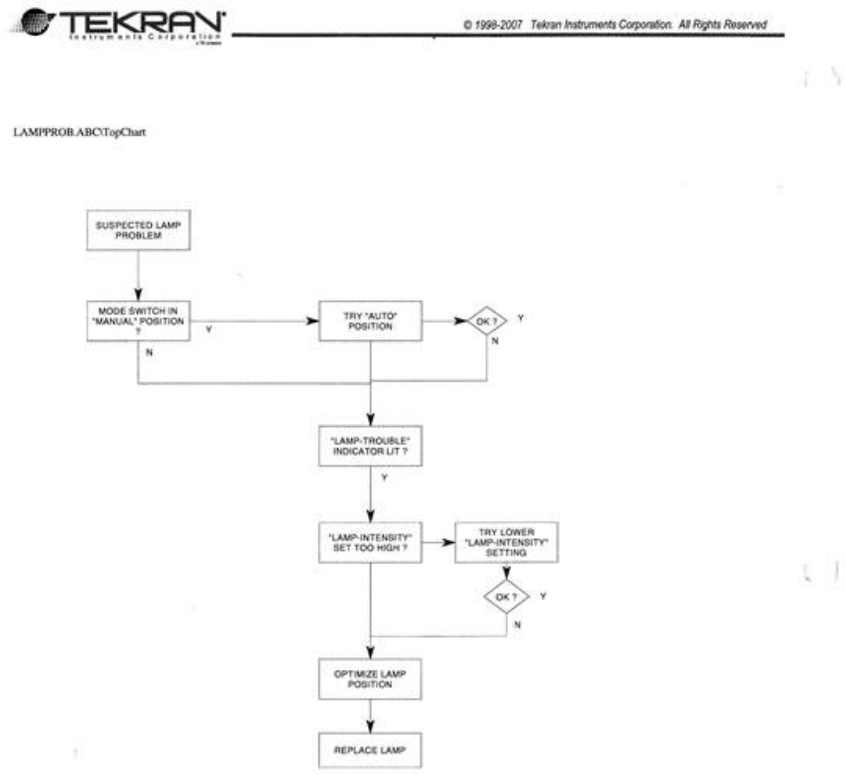


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EFGS-P-DR-SOP2801 Data Review and Validation and Monthly Logbook Reviews
EFGS-Q-QD-SOP2710 Class 1 Weight Calibration, Balance Verification, Calibration & Maintenance
EFGS-Q-QD-SOP41510 Volumetric Verification and Pipette and Dispenser Operation & Maintenance
EFGS-Q-QM-QM5805 Quality Assurance Manual
EFGS-S-CS-SOP2794 Ultra-Clean Aqueous Sample Collection
EFGS-S-HS-QP12066.0004 Chemical Hygiene Plan
EFGS-S-HS-SOP2991 Waste Disposal Procedures for Client Sample Waste
EFGS-S-IT-WI7061 Eurofins Frontier Global Sciences - Instrument and Instrument Software Inventory
EFGS-S-SB-SOP5139 Cleaning of Sampling Equipment and Bottles for Trace Metals Analysis
EFGS-T-AFS-SOP2795 Digestion of Tissues for Total Mercury Analysis Using Nitric Acid and Sulfuric Acids (70:30)
EFGS-T-AFS-SOP2800 Digestion of KCl Traps for Total Mercury
EFGS-T-AFS-SOP2985 Digestion for Gas/Air Samples Collected on Fluegas Sorbent for Total Mercury™ Traps
EFGS-T-AFS-SOP2992 Mercury in Water by Oxidation, Purge & Trap and CV-AFS (EPA Method 1631, Rev E)

EFGS-T-TM-SOP2807 Preparation of Solids Samples for Total Mercury Analysis by Modified Cold Aqua-Regia Digestion
EFGS-T-TM-SOP2821 HF/HNO3/HCl Microwave Digestion of Solids Followed by Repeated HNO3 Evaporation for Trace Metals
EFGS-T-TM-SOP2837 Total Recoverable Metals Digestion for Solid, Animal or Plant Materials
EFGS-T-TM-SOP2839 Stock and Prepared Standards

End of document

Version history

Version	Approval	Revision information	
7.2	06.JAN.2023		
7.3	11.MAY.2023		
8	08.FEB.2024		

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eurofins	Always check on-line for validity.	Level:
	Determination of Trace Metals by ICPMS	**Standard Operating Procedure**
Document number: **EFGS-T-TM-SOP5135**		
Old Reference: **FGS-054**		
Version: **16**		Organisation level: **4-Business Unit**
Approved by: **GW2R** Effective Date: **31-JUL-2024**	Document users: **EFGS_TraceMetal**	Responsible: **EFGS_SMM**

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DOCUMENT IS NOT CONTROLLED WHEN PRINTED

1) Revision Log:
2) Reference:
3) Cross Reference:
4) Purpose:
5) Scope:
6) Basic Principles:
7) Reference Modifications:
8) Definitions:
9) Interferences:
10) Safety Precautions, Pollution Prevention and Waste Handling:
11) Personnel Training and Qualifications:
12) Sample Collection, Preservation, and Handling:
13) Apparatus and Equipment:
14) Reagents and Standards:
15) Calibration:
16) Procedure:
17) Calculations:
18) Statistical Information/Method Performance:
19) Quality Assurance/Quality Control:
20) Corrective Action
21) List of Attachments

1) Revision Log:

Revision: 16	**Effective Date:** This version	
Section	**Justification**	**Changes**
Throughout	Updated	Updated company to Eurofins Seattle.
Throughout	Updated	Removed instructions regarding 1640 analysis.
Throughout	Updated	Added information for analyzing samples by EPA 6020B
2	Added	Added 6020B reference
4	Updated	Updated purpose to include reference methods
7.2	Updated	Changed internal standard recovery.
7.2	Updated	Elements added to "Elements run by method."
7.2	Updated	Removed statement on AS/ASD.
7.2	Updated	Updated recovery limits to match 200.8 and 6020B
7.3	Updated	Performing MDL studies in lieu of IDL studies for 6020B
8	Added	Added definitions for ICSA/ICSAB
8.2	Updated	Changed batch definition.
8.10	Updated	Removed acceptance criteria
10	Updated	Removed HF
12.3	Updated	Updated tissue/solid storage temperature
12.6	Updated	Changed storage time.
13.1	Updated	Updated computer and LIMS requirement.

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Revision: 16	**Effective Date:** This version	
13.1.1	Updated	Removed ISIS for sample introduction
14	Updated	Removed Hydrofluoric Acid and updated section numbers.
14	Updated	Removed high calibration and low calibration standards.
14.5.5	Updated	Reworded internal standard recommendation for germanium
14.5.6	Updated	Removed ICV creation instructions
14.5.6.1	Updated	Changed expiration language to match source method.
14.6	Added	Added interference check solution stock
15	Updated	Calibration requirements added and section numbers updated.
15.4	Added	Added 6020B requirements for calibration point recoveries
15.10	Added	Added ICSA/ICSAB requirement following calibration verification
16.1.1	Added	Removed semiquantitative screening
16.2.1.1	Updated	Order of initialization changed.
16.2.1.2	Updated	Software name changed.
16.2.1.3	Updated	Instruction removed and new instruction added.
16.2.3.7	Updated	Changed solution that carrier probe is placed in.
16.2.3.8	Updated	Changed disposal method.
16.2.3	Updated	Removed section, updated section numbers.
16.2.4	Updated	Removed sections on documenting vacuum pressure.
16.2.5.5	Updated	Changed how to add Hardware Tune to queue.
16.2.5.10	Updated	Changed instructions on where to find files.
16.2.6.1	Updated	Removed instruction on using I.S. line.
16.2.6.4	Updated	Added tune requirement.
16.2.6.9	Updated	Removed section.
16.2.2	Updated	Changed pathway to disable autosampler.
16.3.3	Updated	Changed pathway to enable autosampler.
16.3.3.2	Updated	Changed number of rinses.
16.3.3.4	Updated	Changed nomenclature.
16.3.3.5	Updated	Removed LLCCV
16.3.10	Updated	Removed section, updated section numbers.
19.2	Updated	Removed checklist information.
19.3	Updated	Calibration requirements added and updated.
19.11	Updated	Replaced section with ICSA/ICSAB acceptance criteria
19.12	Updated	Added post-spike and dilution test to required quality control samples
19.13	Updated	Added recommendations for internal standard masses and recovery limits
21	Updated	Removed information on calibration curve preparation.

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Revision: 16	**Effective Date:** This version	
21 Appendix A	Updated	Removed information on reagent preparation.

Revision: 15	**Effective Date: 09/10/2021**	
Section	**Justification**	**Changes**
9.3.3	Updated	Added Polycarbonate and tartaric acid to interference section.

2) Reference:

2.1 Environmental Monitoring Systems Laboratory, EPA Method 200.8, "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry", Revision 5.4, 1994.

2.2 Environmental Monitoring Systems Laboratory, EPA Method 200.8, "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry", Revision 5.5, 1998.

2.3 EPA Method 1638, January 1996.

2.4 AOAC 993.14 Trace Element in Waters and Wastewater ICP-MS, 1993.

2.5 Software Guide – Agilent 8900 Triple Quad ICP-MS, Mass Hunter Workstation User Guide, Agilent Part Number G7201-90601 Revision A, June 2017.

2.6 Hardware Guide – Agilent 8900 Triple Quad ICP-MS, Hardware Maintenance, Agilent Part Number G3666-90001 Revision A, June 2017

2.7 ESI Guide– SC-DX Autosampler Installation Guide, Elemental Scientific, 1500 North 24th Street, Omaha, NE 68110.

2.8 ISIS 3 Guide – Agilent ICP-MS ISIS 3 (Integrated Sample Introduction System), Agilent Part Number G8411-90023 Revision A, June 2017.

2.9 TNI Environmental Laboratory Sector, Vol 1, Management and Technical Requirements, ELV1-2016.

2.10 Department of Defense / Department of Energy Consolidated Quality Systems Manual for Environmental Laboratories, prepared by DoD Environmental Data Quality Workgroup (EDQW) and DOE Consolidate Audit Program (DOECAP) Operations Team, Version 5.3, December 2019.

2.11 EPA Method 6020B (Revision 2), July 2014.

3) Cross Reference:

Document	Document Title
EFGS-Q-QD-SOP41510	Volumetric Verification and Pipette and Dispenser Operation & Maintenance

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Document	Document Title
EFGS-S-CS-SOP2794	Ultra-Clean Aqueous Sample Collection
EFGS-P-SP-SOP2798	Ultra-Clean Sample Filtration
EFGS-T-TM-SOP2836	Total Recoverable Metals in Waters and Aqueous Ceutical Samples by Oven Heating
EFGS-T-TM-SOP2837	Total Recoverable Metals Digestion for Solid, Animal or Plant Materials
EFGS-T-TM-SOP2840	Total Recoverable Metals in Sediments and Soils via a Modified Cold Aqua-Regia Digestion
EFGS-S-SB-SOP5139	Cleaning of Sampling Equipment and Bottles for Analysis of Trace Metals
EFGS-S-HS-SOP2991	Waste Disposal Procedure for Client Sample Waste
EFGS-T-AFS-SOP2821	HF/HNO_3/HCl Microwave Digestion of Solids for Total Mercury
EFGS-S-HS-SOP5670	Health and Safety Evaluation and Auditing
EFGS-T-TM-SOP2825	Total Recoverable Metals Using Nitric Acid Oven Bomb Digestion
EFGS-T-TM-SOP5145	Total Recoverable Metals in Solids via Microwave Oven Digestion
EFGS-Q-QM-QM5805	Quality Manual
EFGS-S-HS-12066	Chemical Hygiene Plan

4) Purpose:

4.1 This SOP describes the method for measuring metals at trace concentrations in water and diluted digested solids by ICP-MS. This procedure outlines steps for reporting in compliance with EPA methods 200.8, 1638, and 6020B (with modifications noted in section 7).

5) Scope:

5.1 This method is used for the determination of dissolved, total, and total recoverable elements in waters and dilute digested solids using inductively coupled plasma - mass spectrometry (ICP-MS). It is intended for use in analyzing low-total dissolved solids (TDS) samples, or samples diluted sufficiently to produce a low-TDS aliquot (ideally, less than 500 mg/L TDS, but no higher than 1,000 mg/L TDS). The calibration range for this method can be from 0.0025 to over 50,000µg/L, depending on the analyte of interest. Method Detection Limit (MDL) studies for all analytes applicable to this method are kept on file in the QA Office.

5.2 This method is written for use with the Agilent 8900 ICP-MS/MS model.

5.2.1 The Agilent 8900 ICP-QQQ is currently equipped with MassHunter 4.4 Workstation Software for ICP-QQQ, VersionC.01.04, Build 544.21, Patch 4 equipped with autosampler software ESI SC Version 2.10 (Compatible with Windows XP, 7, 8, 10).

5.3 This method should be followed to ensure the accuracy and reproducibility of the sample results generated by all ICP-MS analysts at Eurofins Seattle. Only fully trained, experienced ICP-MS analysts, or those under the direct supervision of an experienced ICP-MS analyst, shall be allowed to use this method. Qualified ICP-MS analysts must be thoroughly trained in the interpretation of spectral and matrix interferences, procedures for their correction, as well as ultra-clean sample handling.

5.4 This method shall be followed to analyze for a very large list of analytes; however, at the time of the creation of this SOP, this method has only been fully validated for the analysis of the following metals: Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Pt, Ru, Sb, Se, Sn, Sr, Ti, Ta, Tl, V, W, and Zn. Research-level analyses that generally follow this method shall

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also be performed for other elements, e.g., rare earth elements, uranium, thorium, phosphorus, lithium, etc.

6) Basic Principles:

6.1 An aliquot of a well-mixed, homogeneous sample is prepared for analysis. For determination of dissolved elements, the sample must be filtered either in the field or in the laboratory through a 0.45µm pre-cleaned filter unit according to ultra-clean sample handling techniques (*EFGS-P-SP-SOP2798*, "Ultra-Clean Sample Filtration"), and then preserved with acid. For the determination of total/total recoverable elements in waters, the samples are prepared by solubilizing the analytes through heating with acid, or extracting the analytes from the sample matrix. Acidification will not be performed only at the request of the project managers for special projects.

6.2 Solid samples shall be analyzed by this method after the appropriate digestion steps. All preparation procedures are detailed in separate SOPs.

6.3 Prepared samples are introduced into radio frequency (RF) plasma where energy-transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially-pumped vacuum interface and separated based on their mass-to-charge ratio (m/z) by a mass spectrometer. The Triple Quadrupole system operates in multiple gas modes and rejects all unwanted masses and ions reducing interference. A solid-state detector detects ions transmitted through the mass analyzer and the resulting current is processed by a data handling system.

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7) Reference Modifications:

7.1 The lab evaluates percent recoveries of its calibration standards instead of percent relative error.

7.2 Comparison of EFGS-T-TM-SOP5135 and EPA 1638:

	EFTM-T-TM-SOP5135	Method 1638
Sample Preparation	Dissolved aqueous samples are preserved with ~0.25% nitric acid. Total recoverable aqueous samples are prepared with ~0.25% nitric acid or ~0.25%nitric acid and 0.5% hydrochloric acid and digested in closed containers, in an oven at 85°C.	Dissolved aqueous samples are preserved with 1% nitric acid. Total recoverable aqueous samples are prepared with 1% nitric acid and 0.5% hydrochloric acid and digested in closed containers, in an oven at 85°C.
Matrices	Can be used for various matrices: waters, dilute digested solids, biological tissues, and geological samples.	For aqueous samples only.
Prep./Analysis Blanks	1638/200.8: Continuing Calibration Blanks and Method Blanks must be < PQL. 6020B: ICB/CCB and method blanks under 1/2 PQL.	Continuing Calibration Blanks and Method Blanks must be < MDL.
Field/Equip. Blanks	Recommended	Recommended
ICV/CCV	ICV (SDS) immediately after calibration CCVs (SDS) every 10 samples	ICV (PDS) immediately after calibration CCVs (PDS) every 10 samples
OPR (LCS)	LCS (PDS or SDS) per 10 (1 OPR (PDS or SDS) per 10)	1 OPR (SDS) per 10
MD	None required but can be added at the request of the project manager or client.	None
MS/MSD	MS/MSD pair per 10, spiked at the mid-level of the calibration range.	MS/MSD pair per 10. Usually in mid-level calibration range but must be at least 1-5 times the PQL.
Elements run by method	Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Pt, Ru, Sb, Se, Sn, Sr, Ta, Ti, Tl, V, W, and Zn.	Ag, Cd, Cu, Pb, Ni, Sb, Se, Tl, and Zn.
Internal Standards	Internal standardization typically consists of Sc, Ge*, In, Pt, Rh. Lu, Li6, Te, Tb, Bi, and Y. Recovery should be 30-150%. *See Section 14.7 regarding Germanium use.	Internal standardization utilizes at least three of the following analytes: Bi, Y, In, Sc and Tb. Recovery must be 60-125%.
	Hardware: Ce, Co, Li, Mg, Th, Y at 1 µg/L	Be, Mg, Co, In, Pb at 100 µg/L

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Daily Tuning Solution	Method: Ce, Co, Li, Mg, Th, Y at 10 µg/L.	
Instrument Calibration	Calibration is based on a minimum 5- point calibration curve with a correlation coefficient (R) = 0.995 using a Linear Thru Zero calibration. Calibration Blank is used in Calibration as stated in 1638 section 18.4.	Calibration is based on a 3-point calibration with a RF of <20%.
Control Limits	ICV/CCV/LCS/LCSD/MS/MSD are set to limits listed in method 200.8 for analysis of aqueous samples by this procedure. ICV/CCV/LCS/LCSD/MS/MSD limits set to limits specified in 6020B for solid/tissue samples analyzed by this procedure.	Element-specific acceptance criteria defined in EPA 1638, Table 2.

7.3 In lieu of IDL studies recommended in EPA 6020B, MDL studies performed during initial method validation, verified quarterly, and recalculated if necessary annually.

8) Definitions:

8.1 Analytical Run – the continuous analysis of one or more batches. An analytical run requires a calibration curve, ICV, ICB, and CCV/CCB every ten samples. An analytical run must conclude with a CCV/CCB.

8.2 Batch – comprising no more than 20 samples unless otherwise specified. A batch must contain one Preparation Blank per 10 samples, one MS/MSD set per 10 samples, and one LCS/LCSD set.

8.3 Calibration Standards (CAL) – a series of standards that will be used to calibrate the instrument, made from a PDS. A calibration blank plus at least five different concentrations are required, beginning with one at or below the PQL concentration.

8.4 Certified Reference Material (CRM) – a standard of known composition that is certified by a recognized authority and representing a sample matrix. It is used to verify the accuracy of a method.

8.5 Control Limit (CL) – the limit of the range of acceptability for the quality control samples.

8.6 Dissolved analyte – the concentration of analyte in water after passing through a 0.45mm membrane filter assembly prior to sample acidification.

8.7 HMI: High Matrix Interface. HMI is a gas phase dilution that uses a dilution gas to reduces the amount of sample from the spray chamber to plasma.

8.8 Filtration Blank (FB) - an aliquot of reagent water that is treated exactly as a sample at the time of filtration. The Filtration Blank is used to determine if method analytes or other interferences are present in the filtration paper and/or apparatus.

8.9 Initial and Continuing Calibration Verification (ICV and CCV) – a standard used to check initial calibration and is prepared from a SDS. This standard is run at mid-level concentration and verifies instrument calibration. It is always followed by an ICB.

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8.10 Initial and Continuing Calibration Blank (ICB and CCB) for evaluation of instrument drift, sensitivity, and contamination. ICB must be analyzed directly after the ICV, and the CCBs every 10 samples immediately after CCVs.

8.11 Low Level Calibration Verification (LCV) – a standard analyzed at the request of a client at the method reporting limit. Control limits are based on the client control limits.

8.12 Internal Standard – an element added at the same concentration to all samples and standards in an analytical batch, and used to correct the relative responses of other method analytes in the sample to account for instrument drift. The internal standard must be an element that is not a sample component.

8.13 Laboratory Control Sample (LCS) – the LCS is processed and analyzed exactly like a sample, and its purpose is to determine whether method performance is within acceptable control limits. The LCS can be a reference material, especially in the case of a solid reference material (e.g., a sediment, fish, etc.), or a reagent water to which known quantities of the method analytes are spiked (Also called an Ongoing Precision Recovery sample (OPR)). A PDS or an SDS is used to spike this solution.

8.14 Linear Dynamic Range (LDR) – the concentration range over which the analytical curve remains linear.

8.15 May: This action, activity, or procedural step is optional.

8.16 May Not: This action, activity, or procedural step is prohibited.

8.17 Method Blank or Preparation Blank – an aliquot of reagent water that is treated exactly as a sample at the time of preparation, including exposure to all lab ware, equipment, reagents, and acids that are used with other samples. The Method Blank is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or apparatus.

8.18 Method Detection Limit (MDL) – the minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero as defined in 40 CFR Part 136, Appendix B.

8.19 Method Duplicate (MD) – a second separate sample, taken from the same source sample and analyzed in the laboratory separately at the request of the client. A MSD may be used as a duplicate.

8.20 Matrix Spike (MS) and Matrix Spike Duplicate (MSD) – designated sample (representative of the batch) is spiked with a known concentration of analytes, ideally at 2-5X the expected sample concentration. In the absence of such information, mid-concentration on the calibration curve is desirable. The PDS or an SDS is used to spike the matrix samples.

8.21 Ongoing Precision Recovery (OPR) - A method blank spiked with known quantities of analytes that is carried through the entire sample preparation procedure . Its purpose is to assure that the results produced by the laboratory remain within the limits specified in the referenced methods for precision and accuracy. See LCS.

8.22 Practical Quantitation Limit (PQL) – minimum concentration necessary for quantitative detection by the given method.

8.23 Primary Dilution Standard (PDS) – a standard that is used to make a series of calibration standards for this method; can also be used for IDOC/CDOC.

8.24 Quality control sample (QCS)—A sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory

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performance with test materials prepared external to the normal preparation process. This sample is analyzed within a batch as an LCS and is performed on a quarterly basis.

8.25 RF–Response Factor, percentage units.

8.26 Shall: This action, activity, or procedure is required.

8.27 Should: This action, activity, or procedure is suggested, but not required.

8.28 Stock Standard Solution (SSS) – a standard of analyte that is purchased from a certified source for the preparation of working standards.

8.29 Secondary Dilution Standard (SDS) – a sample of standard from an alternate SSS, used to prepare the ICV, CCV, LCS, LCSD, OPR, MS, and MSD standards, and can also be used for IDOC/CDOC.

8.30 Total analyte – the concentration of analyte in water after digestion in a 2% 9:1 HNO3:HF mix.

8.31 Total recoverable analyte – the concentration of analyte in water after digestion in ~0.25% HNO3 or ~0.25% HNO3 and 0.5% HCl.

8.32 Interference check solution A (ICSA) - a solution containing known interfering elements meant to evaluate the adequacy of instrument interference reduction technology.

8.33 Interference check solution AB (ICSAB) - solution containing known interfering elements and target elements meant to evaluate the adequacy of target element quantitation in the presence of potential interference.

9) Interferences:

9.1 Isobaric Elemental Interference and Polyatomic Isobaric Interference

9.1.1 Q1 (Quadrupole 1) operates as a mass filter rejecting unwanted ions using collision reaction before they reach the (ORS) reaction chamber reducing and/or eliminating interference. The ORS (Octopole Reaction System) is equipped with five gas modes, which when applied correctly will also reduce and/or eliminate interference. Q2 (Quadrupole 2) operates as a second mass filter selecting only to target analyte ions.

9.2 Abundance Sensitivity

9.2.1 The potential for "wing overlap" interference exists when small m/z peaks are being measured adjacent to large ones. If the spectrometer resolution is optimized during tuning, this potential interference is minimized. Note: resolution at 0.700 ± 0.030 units is required.

9.2.2 Select the most abundant isotopes of each analyte.

9.3 Physical Interference

9.3.1 Physical interference results in differences between instrument responses for the sample and the calibration standards. They are associated with the processes related to the transport of the sample into the plasma and the transmission of ions through the interface.

9.3.2 Common physical interferences include viscosity changes, surface tension variability, changes in temperature of the plasma, and varying levels of dissolved solids. The use of internal standards effectively reduces the effects from most physical interferences.

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9.3.3 Avoid the use of Polycarbonate. Carbon is slowly leached out causing a bias on chromium and other elements affected by carbon. Avoid the use of tartaric acid in general and as a preservative in all purchased stock standards. This can cause Silver to precipitate out, leading to failing CCV's.

9.4 Carryover

9.4.1 Memory effects on the probe, nebulizer, mixing block, cones, torch, spray chamber, and autosampler are minimized by flushing the system with a rinse blank between samples (see 14.2.6). Some analytes have more severe memory effects than others (e.g. B, Mo, Ag, Hg and Sb) so special care must be taken when determining these elements.

9.4.2 If carryover interference is suspected, the sample must be reanalyzed at an alternate dilution after a rinse, under the same analytical conditions of the analytical run or after the analysis of an acceptable blank (less than the PQL). Each rinse is to be treated as a discreet injection.

10) Safety Precautions, Pollution Prevention and Waste Handling:

10.1 Personnel will don appropriate laboratory attire according to Chemical Hygiene Plan (CHP) *EFGS-S-HS-12066*. This may include, but is not limited to: laboratory coat, apron, eye protection, face shield and protective gloves.

10.2 The toxicity or carcinogenicity of each laboratory reagent has not been fully established. Therefore, every chemical must be treated as a potential health hazard. Exposures shall be reduced as much as possible. Analysts and technicians are expected to familiarize themselves with the characteristics and risks of each chemical they work with by referring to the SDS located at https://msdsmanagement.msdsonline.com/company/5c1df5b3-747d-4789-8104-42457dc3a3e5/

10.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease-causative agents. Eurofins Seattle will reimburse the expense of Hepatitis A and B immunizations for any laboratory staff member who desires this protection.

10.4 Nitric acid (HNO3): Corrosive. Strong oxidizer. Contact with other material may cause a fire. Causes eye and skin burns. May cause severe respiratory tract irritation with possible burns. May cause severe digestive tract irritation with possible burns.

10.4.1 Eye Contact

10.4.1.1 Causes severe eye burns. Direct contact with liquid may cause blindness or permanent eye damage.

10.4.2 Skin Contact

10.4.2.1 Causes skin burns. May cause deep, penetrating ulcers of the skin. Concentrated nitric acid dyes human skin yellow on contact.

10.4.3 Inhalation

10.4.3.1 Effects may be delayed. Causes chemical burns to the respiratory tract. Inhalation may be fatal as a result of spasm, inflammation, edema of the larynx and bronchi, chemical pneumonitis and pulmonary edema. Aspiration may lead to pulmonary edema. May cause systemic effects. May cause acute pulmonary edema, asphyxia, chemical pneumonitis, and upper airway obstruction caused by edema. Depending on the conditions, the vapor or fumes of nitric acid may actually be a mixture of nitric acid and

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various oxides of nitrogen. The composition may vary with temperature, humidity, and contact with other organic materials.

10.4.4 Ingestion

10.4.4.1 May cause severe and permanent damage to the digestive tract. Causes gastrointestinal tract burns. May cause perforation of the digestive tract. May cause systemic effects.

10.4.5 Chronic

10.4.5.1 Exposure to high concentrations of nitric acid vapor may cause pneumonitis and pulmonary edema which may be fatal. Symptoms may or may not be delayed. Continued exposure to the vapor & mist of nitric acid may result in a chronic bronchitis, & more severe exposure results in a chemical pneumonitis. The vapor & mists of nitric acid may erode the teeth, particularly affecting the canines & incisors.

10.5 Hydrochloric acid: Very hazardous in case of skin contact (corrosive, irritant, permeator), of eye contact (irritant, corrosive), of ingestion. Slightly hazardous in case of inhalation (lung sensitizer). Non-corrosive for lungs. Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. Severe overexposure can result in death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

10.5.1 Eye Contact:

10.5.1.1 Check for and remove any contact lenses (contact lenses shall never be worn in the laboratory). In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention immediately.

10.5.2 Skin Contact:

10.5.2.1 In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Cover the irritated skin with an emollient. Cold water may be used. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention immediately.

10.5.3 Serious Skin Contact:

10.5.3.1 Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek immediate medical attention.

10.5.4 Inhalation:

10.5.4.1 If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention immediately.

10.5.5 Serious Inhalation:

10.5.5.1 Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. WARNING: It may be hazardous to the person providing aid to give mouth-to-mouth resuscitation when the inhaled material is toxic, infectious or corrosive. Seek immediate medical attention.

10.5.6 Ingestion:

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10.5.6.1 If swallowed, do not induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention immediately.

10.6 See Eurofins Seattle Chemical Hygiene Plan (CHP) for general information regarding employee safety, waste management, and pollution prevention.

10.7 Pollution prevention information can be found in the current Eurofins Seattle Chemical Hygiene Plan (CHP), which details and tracks various waste streams and disposal procedures.

10.8 All laboratory waste is accumulated, managed, and disposed of in accordance with all federal, state, and local laws and regulations. Any waste generated by this procedure should be disposed of according to SOP *EFGS-S-HS-SOP2991* "Waste Disposal Procedure for Client Sample Waste," which provides instruction on dealing with laboratory and client waste.

11) Personnel Training and Qualifications:

11.1 An analyst must perform an initial demonstration of capability (IDOC) that includes four replicates of a secondary source before being qualified to analyze samples without supervision. Continuing DOC will be maintained and monitored via performance on QC samples.

11.2 Training is documented by the employee and supervisor, and is kept on file in the QA Office. The employee must read, understand, and by signing the training document, agree to perform the procedures as stated in all Standard Operating Procedures (SOPs) related to this method.

11.3 All employees must also read the Quality Manual (QM) and complete yearly Ethics training.

11.4 All training documents including IDOCs, CDOCs, Initial QA orientation, and Ethics training are stored by the Quality Assurance Manager in the employees training file for ten years after the employee is no longer working for Eurofins Seattle.

11.5 Chemical Safety Training, Compressed Gas Training, Chemical Hygiene Plan documentation, and Shipping of Hazardous goods, are stored by the Health and Safety Officer for ten years after the employee is no longer working for Eurofins Seattle.

12) Sample Collection, Preservation, and Handling:

12.1 All aqueous samples must be collected according to the protocols described in SOP *EFGS-S-CS-SOP2794*, "Ultra Clean Aqueous Sample Collection" (equivalent to EPA 1669). Solid samples must be collected in polyethylene or fluoropolymer jars.

12.2 Samples for dissolved metals determination must be filtered through a 0.45mm or a 0.2mm pre-cleaned disposable filter unit. Eurofins Seattle recommends that the samples shall be filtered at the laboratory within 48-hours of sample collection and prior to preservation, if the samples are not filtered in the field as per EPA requirements. Filtering procedures are described in SOP *EFGS-P-SP-SOP2798*, "Ultra-Clean Sample Filtration."

12.3 Aqueous samples must be preserved to an acidity of pH 2 or less, see Section 12.8 for non-preserved samples. Solid samples require no preservation; however, refrigeration at -11°C or lower is required for soil and/or biological tissue samples. Other solid samples may be stored at room temperature. In general, one of the following preservation schemes is followed for aqueous samples.

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12.3.1 Preserve to ~0.25% v/v with HNO3 for total recoverable metals digestions (SOP *EFGS-T-TM-SOP2836* "Total Recoverable Metals Digestion by Oven Heating").

12.3.2 For dissolved metals determinations, preserve filtered sample with same acid as 'total' partner in either specifics can be found in SOP *EFGS-T-TM-SOP2836*.

12.4 When preserving samples, the pipette tip must be pre-cleaned with ~2-5% HNO3 prior to the pipetting of acids.

12.5 1638 Preservation: Preserved samples must be stored for a minimum of 48 hours at 0-4° Celsius before preparation and/or analysis to completely dissolve the metals adsorbed on the bottle walls. Preserved samples must be must be stored in a secure area of the laboratory.

12.6 200.8 Preservation: Preserved samples must be stored for a minimum of 24 hours at room temperature before preparation and/or analysis to completely dissolve the metals adsorbed on the bottle walls. Preserved samples must be must be stored in a secure area of the laboratory.

12.7 Clients requesting acid soluble samples must be preserved for a minimum of 16 hours and filtered through a pre-cleaned filter and labeled acid soluble.

12.8 Preservation will not be performed only at the request of the project managers or Trace Metals Leads for special projects. Samples that have not been preserved will be stored 0-4° Celsius until digestion/analysis and must be stored in a secure area of the laboratory. Refer to SOP *EFGS-T-TM-SOP2836* for digestion modification.

13) Apparatus and Equipment:

13.1 LIMS – TALS (current production version); Computer equipped with Windows 10 (or higher).

13.2 Facility: A clean laboratory environment is crucial to the success of producing good data for ultra-low levels of trace metals. All sample preparation must take place in a clean hood (Class-100), whenever possible. Adhesive mats must be used at all entry points to the laboratory to control dust and dirt from shoes. Fume hoods must be non-metallic. Clean-room gloves (Class-100) must be changed whenever contact is made with anything not known to be trace-metal free.

13.3 Instrumentation:

13.3.1 Agilent 8900 ICP-MS Triple Quad

13.3.1.1 Software: MassHunter 4.4 Workstation Software for ICP-QQQ, VersionC.01.04, Build 544.21, Patch 4.

13.3.2 Autosampler: ESI SC-14DX

13.3.2.1 Software: ESI SC Version 2.9.0388 (Compatible with Windows XP, 7, 8, 10.)

13.4 Other Apparatus and Materials:

13.4.1 Analytical balance capable of measuring to 0.1mg

13.4.2 Convection oven capable of maintaining 85°C (± 3°C)

13.4.3 pH paper, range 1-11

13.4.4 Sample bottles – can be constructed of fluoropolymer (FEP, PTFE), polyethylene (HDPE, LDPE), polycarbonate (PC), polypropylene (PP), or glass. All bottles must be cleaned according to SOP *EFGS-S-SB-SOP5139*, "Cleaning of Sampling Equipment and Bottles for Analysis of

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Trace Metals." Glass must not be used with HF, or for analyses requiring measurement of Si, B, Al, alkaline, or alkaline-earth metals.

13.4.4.1 PC is not recommended for long term storage.

13.4.5 Clean-room gloves, Class-100 (non-latex)

13.4.6 Autosampler vials: 50mL Centrifuge tubes pre-cleaned for Zinc only from certain vendors. All other metals can be used from the vendor packaging after 3 rinses with reagent water.

13.4.7 Plastic zip-type bags, various sizes

13.4.8 Volumetric flasks, Class-A (cleaned according to SOP *EFGS-S-SB-SOP5139*, "Cleaning of Sampling Equipment and Bottles for Analysis of Trace Metals"), Glass volumetric flasks can only be used for preparation and not storage. The preparation of Si, B, Al, alkaline, or alkaline-earth metals in pre-cleaned glass containers is strictly prohibited.

13.4.9 Assorted calibrated pipettes (calibrated according to SOPs *EFGS-Q-QD-SOP41510*, "Pipette Verification, Calibration & Maintenance" and EFGS-155, "Calibration of Volumetric Dispensers").

13.4.10 Solution storage bottles, 125mL to 2000mL, from any of the above plastics excluding polycarbonate (PC) due to the leaching of Carbon over time.

13.4.11 Disposable filter units, 150mL to 500mL, pre-cleaned

13.4.12 Vacuum pump and tubing connections for filtering

13.4.13 Peristaltic Pump tubing: Flared end PVC 3 stop tubing

13.4.13.1 Blue and Orange tabs with 0.25 mm ID Part: 0.25-0B3B-F from Glass Expansion or equivalent for I.S.

13.4.13.2 White Tabs with 1.02 mm ID for Carrier, Part: 1.02-WHT3B-F from Glass Expansion or equivalent.

13.4.13.3 Santoprene 2 stop tubing for waste.

14) Reagents and Standards:

14.1 Reagents may contain elemental impurities that could affect the integrity of analytical data. Because of the high sensitivity of ICP-MS, high-purity reagents must be used. (The highest grade does not necessarily mean a reagent has the lowest trace element concentration.) Each reagent lot must be tested for the metals of interest.

14.2 Reagent Water: 18-MΩ ultra pure deionized water starting from a pre-purified (distilled, R.O., etc.) source is ued. To remove any remaining trace metals and organics, an activated carbon cartridge is placed between the final ion exchange bed and the 0.2-µm filter. The reagent water is tested for trace metal and mercury concentrations on a monthly basis and must test less than the ½ the PQL to be in-control.

14.3 Nitric Acid (HNO3): Concentrated (69%-70% weight basis) low trace-metal grade nitric acid. Several brands (Baker, Fisher, Omnitrace) have been found to have lots with acceptably low levels of trace metals. This reagent should be from a lot number that has been previously tested to be low for

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the analytes of interest. This reagent shall be entered into LIMS and the expiration date is set to 3 years after receipt date.

14.3.1 ~2% (v/v) HNO3 – used for soaking autosampler tubes from certain vendors and storing bottles and volumetric flasks when not in use.

14.3.2 3% (v/v) HNO3 – used to prepare primary and secondary dilution standards, prepared fresh daily.

14.3.3 ~5% (v\v) HNO3 – used to rinse pipette tips and clean Sampler and Skimmer Cones

14.3.3.1 Rinse bottle labeled:

Metals Rinse, 5% HNO3

To be used for CV-AFS (THg only) and ICPMS preps/analysis.

14.3.4 10% (v\v) HNO3–used to prepare calibration standards, for primary and secondary dilution standard, sample preparation diluents, prepared fresh daily.

14.4 Hydrochloric Acid (HCl): Concentrated (36.5%-38.0% weight basis) low trace-metals grade hydrochloric acid. Several brands (Baker, Fisher, Omnitrace) have been found to have lots with acceptably low levels of trace metals. This reagent must be from a lot number that has been previously tested to be low for the analytes of interest. This reagent shall be entered into LIMS and the expiration date is set to 3 years after receipt date.

14.4.1 2% (v/v) HNO3/0.5% HCl– used to prepare calibration standards, for primary and secondary dilution standard, sample preparation diluents, prepared fresh daily.

14.4.2 15% (v/v) HNO3/0.5% HCl– used to prepare rinse and standards, prepared fresh daily.

14.5 Trace Metals Stock and Prepared Standards

14.5.1 See SOP EFGS-T-TM-SOP2839 for information regarding the receipt, documentation, preparation, and storage of purchased and prepared standards used by Eurofins Seattle.

14.5.2 It is suggested to have a single element standard for each of the commonly determined metals as well as any metals that shall be used as internal standards or interference check samples.

14.5.3 Optimization Standards

14.5.3.1 Tuning Stock Solution: Add 50µL each of the following 1000ppm standards to a 50mL centrifuge tube: Yttrium, Cobalt, Thallium, Cerium, Lithium 6 and Magnesium. Bring to a final volume of 50mL with 3% HNO3. This solution has an expiration of twelve months or the earliest expiration of the stock standard and may be prepared at an alternate volume as long as the ratio is kept the same.

14.5.3.2 ICPMS Agilent Hardware Solution: Add 500uL of Tuning Stock Solution to a clean 500mL volumetric flask and bring to final volume of 500mL with 3% HNO3. Transfer to a clean poly or Teflon container. This solution has an expiration of twelve months or the earliest expiration of the stock standard and may be prepared at an alternate volume as long as the ratio is kept the same.

14.5.3.3 ICPMS Agilent Software solution (Method Tune solution): Add 5mL of Tuning Stock Solution to a clean 500mL volumetric flask and bring to final volume of 500mL with 3% HNO3. Transfer to a clean poly or Teflon container. This solution has an expiration

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of twelve months or the earliest expiration of the stock standard and may be prepared at an alternate volume as long as the ratio is kept the same.

14.5.4 Calibration Standards (prepped from Primary Stock Standards).

14.5.4.1 Calibration Curve: Dilute a multi-element stock standard solution consisting of target elements in pre-cleaned 50mL autosampler vials with 2% HNO3/0.5% HCL for waters analysis or 10% HNO3 for solids. Curve matrix is determined by type of sample matrix. As per Laboratory Manager or a Project Manager request, an alternate curve can be used to achieve lower detection limits or extending the linear range. Calibration standards expire when one or more of the stock standards has expired and may be prepared at alternate volumes if necessary as long as the ratios are kept consistent.

14.6.4.1.1 Additional elements (such as Hg, Rb, Li, Th, Os, W, etc.) shall be prepared as a separate standard to be added to any of the above the curves, if care is taken to avoid incompatibility issues and internal standard conflicts.

14.5.5 Internal Standards:

14.5.5.1 Internal standard solution – dilute stock standard solutions of the elements in table below in 2% (v/v) HNO3/0.5% HCl. Below are suggested analytes and concentrations. Instrument response for these elements should fall within 100,000-900,000 counts per second (cps). If the cps fall outside of this range, it is suggested the concentration be adjusted until the range has been reached. This solution is stable at the earliest expiration of the standards used. Alternate internal standards shall be chosen based on sample matrix, on-going research, and specific analytical requests. The Internal standard is added via peristaltic pump to all standards and samples.

Ge: 10.00 mg/L	Re: 1.00 mg/L
Li6 15.00 mg/L	Sc 1.00 mg/L
In: 0.60 mg/L	Tb: 1.00 mg/L
Lu: 0.40 mg/L	Pt: 15.00 mg/L
Bi: 0.625 mg/L	Y: 0.25 mg/L
Tm: 0.40 mg/L	Rh: 0.50 mg/L
Te: 0.40 mg/L	

Note: Use of Germanium is not recommended when Arsenic is analyzed in Helium mode.

14.5.6 ICV/CCV – Initial and continuing calibration verification solution (prepped from secondary stock solutions)

14.5.6.1 ICV/CCV is used to verify the validity of the calibration curve and must be analyzed immediately following the calibration curve and then after every 10 samples throughout the run. The ICV/CCV used shall vary depending on the analytes being

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measured, and is left to the discretion of the analyst. The most common ICV/CCV used is listed below. The calibration verification standards may be prepared at alternate volumes if necessary as long as the ratios are kept consistent. New ICV/CCV should be prepared every two weeks or as needed.

14.5.7 Certified reference materials of various waters (e.g., river water, seawater, estuarine water, etc.).

14.5.8 Quality control sample (QCS)—The QCS must be prepared from an alternate source than was used to produce the calibration standards. The calibration standards and acceptable instrument performance must be verified with the preparation and analyses of a QCS on quarterly basis.

14.6 Interference check solution stock solution: Solution containing commonly interfering elements at the following suggested concentrations:

- Mo and Ti at 20 ppm
- Al, Ca, Fe, K, Mg, Na, P, and S at 1000 ppm
- C at 2000 ppm
- Cl at 10000 ppm

15) Calibration:

15.1 After instrument optimization, the calibration standards described in section 14.6.4 are analyzed.

15.2 Calibration is based on a minimum 5-point calibration curve with a correlation coefficient (R) = 0.995 using a Linear Thru Zero calibration.

15.3 The first calibration standard shall be at or below the PQL.

15.4 When analyzing samples by EPA 1638 or 200.8, the recovery of all calibration points must be between 50% and 150%. When analyzing samples by EPA 6020B, the recovery of the top two calibration points must be between 90% and 110% and all other calibration points must recover between 80% and 120%.

15.5 When quantitated using the calibration, the concentration axis intercept shall be below the PQL.

15.6 Individual analyte calibration levels can be removed from the lowest and/or highest levels of the curve. Multiple levels may be removed, but removal of interior levels is not permitted. The LOQ/reporting limit and quantitation range of the calibration based on the concentration of the remaining high and low calibration standards should be adjusted accordingly.

15.7 An entire single standard calibration level from the interior of the calibration curve can be removed when the instrument response demonstrates that the standard was not properly introduced to the instrument or an incorrect standard was analyzed, provided that the level is removed for all analytes. Removal of calibration points from the interior of the curve is not to be used to compensate for lack of maintenance or repair to the instrument.

15.8 A single calibration standard can be replaced provided that the laboratory analyzes the replacement standard before the ICV is analyzed (which meets the TNI requirement that it must be

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analyzed within twenty-four (24) hours of the original calibration standard analysis for that particular calibration level) and that all analytes of an interior standard are replaced.

15.9 The reason for removing or replacing an interior standards must be technically valid and documented.

15.10 If running samples by EPA 6020B, an ICSA and ICSAB solution must be run after the instrument calibration and ICV/ICB. The ICSA is typically prepared as a 100x dilution of the interference check solution stock. The ICSAB is prepared with the same concentration of interference check solution stock as the ICSA and target analytes spiked at approximately the calibration mid-point or lower.

16) Procedure:

16.1 Sample Preparation:

16.1.1 For the determination of total and total recoverable analytes, there are several different preparation procedures to choose from. The decision of which method to use is based on the client's needs and requests, the required MDLs, the matrix of the sample, and how the data will be used.

16.1.1.1 Refer to SOP *EFGS-T-TM-SOP2836* (Digestion for Total Recoverable Metals in Waters by Oven Heating) for procedures on digesting fresh waters with metals levels above ambient levels, sea or wastewaters with high levels of metals (amenable to dilution).

16.1.1.2 Refer to SOP *EFGS-T-TM-SOP2837* (Total Recoverable Metals Digestion for Solid, Animal or Plant Materials) for applicable procedures.

16.1.1.3 Refer to SOP *EFGS-T-AFS-SOP2821* (HF/HNO3/ HCl Bomb Digestion of Solids for Total Mercury Followed by Repeated HNO3 Evaporation for Other Metals) for applicable procedures.

16.1.1.4 Refer to SOP *EFGS-T-TM-SOP2840* (Total Recoverable Metals in Sediments and Soils via a Modified Aqua Regia Oven Bomb Digestion) for applicable procedures.

16.1.2 For determination of dissolved elements, samples must be acidified, following filtration. If the samples are suspected to be high in metals or dissolved solids, they must be diluted with 15% HNO3/0.5%HCL to achieve an approximate TDS level in the diluted sample of 500-1000mg/L.

16.2 Instrument Start up and Optimization:

16.2.1 Start-up: Restart computer on a daily basis to ensure all updates are installed properly.

16.2.1.1 The instrument software must be opened and initialized before the ESI software.

16.2.1.2 Open ICP-MS Instrument Control.

16.2.1.3 Then open ESI SC. Initialize autosampler and change the loop size to 2.0mL.

16.2.2 Disable the Autosampler- Click on the Autosampler icon. Uncheck the Use Autosampler box.

16.2.3 Inspect instrument parts and set up for analysis:

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16.2.3.1 Check the gas supply to be sure they are at operating levels.

16.2.3.1.1 Argon gas pressure: 500 to 700 kPa

16.2.3.1.2 Cell gas (Helium): 90 to 130 kPa

16.2.3.1.3 Cell gas (Hydrogen) and (Oxygen): 20 to 60 kPa

16.2.3.2 Check to ensure exhaust duct is properly connected and cooling water is at sufficient levels.

16.2.3.3 Check sampler and skimmer cones. Clean or replace as needed.

16.2.3.4 Check the plasma torch for clogging deposits or chips. Replace if severe wear is noted.

16.2.3.5 Inspect the RF load coil and injector for discoloration and distortions. Realign if necessary. Once checked or adjusted verify that alignment is still intact.

16.2.3.6 Replace carrier and Internal Standard pump tubing on an as needed basis. Keep tubes unclamped when not in use to preserve tubing. Waste tubing shall be replaced as needed.

16.2.3.7 Clamp tubing and ensure carrier line, I.S. line, and waste line are hooked up correctly, and in the Instrument tune configuration. Carrier probe should be placed in 10% HNO3 for warm up sequence and carrier line should be hooked up directly to the nebulizer through the peristaltic pump. I.S. line should be disconnected.

16.2.3.8 Check the level of the sample waste container, if full, dispose in proper waste stream.

16.2.3.9 Check oil level and color. When it is pink/red it is time to replace. MassHunter will prompt you to change oil every 6 months.

16.2.4 Light Plasma:

16.2.4.1 Ignite plasma by clicking on the Plasma dropdown menu and selecting Plasma On. Make sure that the checkbox for Execute Configured Ignition Sequence is checked and click OK.

16.2.4.2 Refer to the Agilent 8900 MassHunter Work Station User Guide for procedures for starting the instrument after an extended shutdown, or after moving or replacing major components.

16.2.5 Hardware Tune:

16.2.5.1 Hardware Tune will start automatically after a ~25 minute warm up.

16.2.5.2 Ensure the Autosampler is disabled before the Hardware Tune begins.

16.2.5.3 Move the carrier probe into the Hardware Tune solution approximately 5 minutes prior to end of warm up.

16.2.5.4 When warm up is complete a window will appear prompting you to introduce sample. Click OK as you have already done this.

16.2.5.5 Manual start of Hardware Tune- If instrument was already on and did not require a warm up the Hardware Tune can be manually started by clicking Startup

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Configuration, selecting the desired parameters (see sections 16.2.5.6/7), and clicking Add To Queue.

16.2.5.6 Daily Hardware Tune- Select the following parameters:

- Torch Axis
- Standard Lens Tune
- Resolution Axis
- Performance Report

16.2.5.7 Monthly Hardware Tune: Do a full optimization, tuning all parameters excluding the P/A Factor at least once monthly.

16.2.5.8 Go to Queue to view the status of the tune. This will display what task is currently running, the status, as well as start and end times.

16.2.5.9 When the tune is complete a new window will appear instructing to Introduce solution for 'Probe Rinse'. Move the carrier probe into Rinse and click OK.

16.2.5.10 Generate Performance Report

16.2.5.10.1 Go to Dashboard located under Hardware.

16.2.5.10.2 Right-click on the mainframe and select Performance Report. This will take a moment to load.

16.2.5.10.3 Select the correct date and time from the dropdown menu and click Generate Report.

16.2.5.10.4 Save the report in D:\Agilent\ICPMH\1\DATA\year\month\ICPMS-YYMMDD\TuneReport in the format ICPMS9-YYMMDD_Performance report number for that date. For example the first performance report generated on October 22, 2019 will be named ICPMS9-191022-1.

16.2.5.10.5 Print out pages 1-5 of the performance report and compare the values with the criteria listed on the Agilent Mandatory Performance Qualification Checklist. Criteria is also listed in table below. These are suggested criteria and are subject to change.

Tune Parameter	Criteria
Li 7 Sensitivity	≥ 4,200 @ 0.1 sec
Y 89 Sensitivity	≥ 16,150 @ 0.1 sec
Th 205 Sensitivity	≥ 5,950 @ 0.1 sec
RSD's for Li7, Y, Th only	≤ 5%
Measured Mass	±0.10
Resolution Width	0.65-0.75

16.2.5.11 If Hardware Tune is passing proceed with Software Tune in the new batch. If Hardware Tune is failing conduct troubleshooting (See page 136-138 of the Hardware Maintenance Manual and ICP-QQQ troubleshooting docs), consult with a lead or manager, and/or rerun Hardware Tune.

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16.2.6 Software Tune (Method Tune):

16.2.6.1 While still in instrument tune configuration, move the carrier probe to the Method Tune Solution.

16.2.6.2 Create new Batch:

16.2.6.2.1 Select desired batch template from the drop down menu on the Create From Template Icon.

16.2.6.2.2 Enter the New Batch Name in the format (YYMMDD)-that day's batch number. For example the first batch created on ICPMS9 on October 22, 2019 would be named ICPMS9-191022-1.

16.2.6.2.3 Make sure batch is set to save in correct folder. For example a batch created on October 22, 2019 would be saved in D:\Agilent\ICPMH\1\DATA\2019\10 - October.

16.2.6.2.4 Click Create.

16.2.6.2.5 Alternatively a previous batch can be opened that contains the parameters desired and resaved as todays batch.

16.2.6.3 Make any desired changes to method and Save batch. DO NOT make any changes to your method after running the Software Tune. For more information on method editing and creation see the MassHunter Workstation User Guide.

16.2.6.4 Select the Tune Modes tab under the Acquisition Method tab

16.2.6.5 Click Start Auto Tune. Select "All Tune Modes" and ensure the Skip PeriPump/ISIS Program box is checked and click OK.

***Note**: You will not be able to do anything in the Instrument Control software while the Method Tune is being performed. It takes ~10 minutes. After the tune no changes should be made to the tune parameters of the batch Acquisition Method.

16.2.6.6 Once the Method Tune is complete the software will automatically create and print a PDF. This PDF is saved in the batch folder.

16.2.6.7 If the tune meets the passing criteria the instrument is ready for Analysis. Criteria is listed on the Agilent Mandatory Performance Qualification Checklist and in the table below. Criteria is suggested and is subject to change.

16.2.6.7.1 Instrument stability must be confirmed by running the tuning solution a minimum of five times. The resulting relative standard deviations of absolute signals for all analytes from a representative mass range (typically 59, 89, and 205) must be less than 5%. Doubly-charged and oxide ratios are evaluated from scanning associated masses through manual calculation.

16.2.6.7.2 Table of Software Tune passing criteria:

Parameter	Requirement
Axis	± 0.1 amu from true value
Resolution	< 0.9 amu at 10% peak height
RSD	RSD ≤ 5%
Oxides	CeO/Ce ≤ 2%
Double-Charged	Ce++/Ce ≤ 3%

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16.2.6.8 If the tune does not meet the passing criteria conduct troubleshooting (See page 136-138 of the Hardware Maintenance Manual and ICP-QQQ troubleshooting docs), consult with a lead or manager, and/or rerun Software Tune.

16.3 Analysis:

16.3.1 Place the Carrier probe into the carrier solution and the I.S. probe into the Internal Standard Solution.

16.3.2 Enable the Autosampler- Click on the Autosampler icon. Uncheck the Use Autosampler box.

16.3.3 Create sample list

16.3.3.1 In the new batch select Sample List.

16.3.3.2 Check that template has included at least 6 rinse/wash, the Calibration blank, the calibration, and ICV/ICB.

16.3.3.3 Add samples below ICV/ICB making sure to add a CCV/CCB after every 10 samples. You can also add an optional pause after the ICV/ICB if you would like to check the curve and ICV before sample analysis begins.

16.3.3.4 Be sure to fill out all columns for all rows to be analyzed.

16.3.3.4.1 Sample Type: Enter CalBlk (ICIS), CalStd (STD#), CCV(ICV/CCV), Blank (CCB/Blank), LCS (LCS/LCSD), or Sample.

16.3.3.4.2 Sample Name: Enter Wash, ICIS, STD#, ICV/ICB/CCV/CCB, LIMS ID, or other description.

16.3.3.4.3 Comment: Enter Batch ID or can be left blank.

16.3.3.4.4 Vial#: Enter autosampler position. See attachment *ESI SC-14 DX Autosampler Positions* for position numbers.

16.3.3.4.5 File name: Leave blank, this will fill in automatically.

16.3.3.4.6 Level:

16.3.3.4.6.1 Calibration blank solution (CalBlk): Select Level 1.

16.3.3.4.6.2 Calibration standard (CalStd): Select Level 2, Level 3, and so on, in ascending order of concentration.

16.3.3.5 Make sure the following guidelines are met:

16.3.3.5.1 Sample results are quantitated from the initial calibration.

16.3.3.5.2 The ICV standard must always immediately follow the calibration curve.

16.3.3.5.3 The initial calibration blank (ICB) must be run immediately after the ICV as an indication of analyte carry-over.

16.3.3.5.4 A continuing calibration verification (CCV) sample shall be the same solution as the ICV solution, and represent the mid-range of the calibration curve. It must be analyzed every 10 samples, and must be run at the conclusion of analysis.

16.3.3.5.5 A continuing calibration blank (CCB) must be analyzed after each CCV to monitor for carry-over.

16.3.3.5.6 For initial batch to be analyzed all LCS/LCSD pairs or OPR, preparation blank(s) and equipment and filter blanks must be analyzed prior to running samples. All other batches can be analyzed in an order most efficient for the batch needs. Note this is for 1638/200.8 water batches that have not been analyzed. Samples requesting reanalysis with passing QC need only analyze ICV/ICB, samples requested for analysis and CCV/CCB pairs per 10 samples.

16.3.3.6 At the end of the run be sure to close off with a final CCV/CCB and a shutdown procedure usually comprised of rinses, DI water, and ending with air.

16.3.4 Click Add to Queue to start analyzing.

16.3.5 Mass Hunter Online Data Analysis will open automatically. Here you can view your data in real time.

16.3.6 If desired, enable the Plasma Off at End option.

16.3.7 To edit Sample List while analyzing highlight any cell below the sample that is currently being analyzed and Click Start editing. When you are finished editing Click Stop Editing. Make sure to finish editing before the first sample that is highlighted comes up in queue.

16.3.8 While Instrument is rinsing load Calibration, ICV/ICB, samples, and any shutdown procedure solutions. Ensure they are in the proper positions set in the Sample List.

16.3.9 Ensure Carrier, I.S., and Rinses are filled.

16.3.10 Once run is complete analytical batch data will be saved in Mass Hunter Offline Data Analysis automatically and available for export. For information regarding data review see SOP *EFGS-P-DR-SOP2801*(Data Review and Validation and Monthly Logbook Reviews).

16.4 Instrument maintenance:

16.4.1 Preventative maintenance – the user shall refer to the Hardware Maintenance Manual, which details extensively all the daily, weekly, and monthly preventative maintenance for the instrument. All maintenance must be documented in the instrument maintenance logbook. Correct instrument optimization is a crucial part of the quality control.

16.4.2 Instrument cones shall be evaluated for sample build up, wear on the cones, pitting and aperture size. Cones should be cleaned with 5% HNO3 if build up has occurred. Care should be taken as the cone is malleable.

16.4.3 Pump tubing shall be evaluated for wear and over compression. Pump tubing should be replaced if any of these signs are observed.

16.4.4 Vacuum oil shall be checked for any color changes. If the oil appears to be red in color it shall be replaced. MassHunter prompts you to change oil every 6 months.

16.4.5 The torch shall be evaluated for deep cracks. If a crack is observed the torch must be replaced.

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17) Calculations:

17.1 Instrument concentrations are calculated by the MassHunter Software.

17.2 Instrument concentrations are imported into a Laboratory information management system and are calculated as follows for a final concentration of ppb.

$$\frac{\{\text{Instrumental Value (µg/L)} * \text{F.V. (mL)} * \text{D.F.}\}}{\{\text{I.V. or Mass (mL or g)}\}}$$

17.3 The values for the calibration standards are recalculated against the newly created calibration curve. The solution is not re-analyzed.

17.4 The samples are not blank corrected.

17.5 Hardness is calculated from separate determinations of calcium and magnesium, according to Standard Method 2340B and ideally from the same analytical run.

Hardness (mg equiv. CaCO3/L) = 2.497 [Ca, mg/L] + 4.118 [Mg, mg/L].

18) Statistical Information/Method Performance:

18.1 Method Detections Limits (MDL) are determined during method development and then annually thereafter according to 40 CFR Part 136, Section B and CA-Q-S-006.

18.2 The Practical Quantitation Limit (PQL) is the reporting limit for this method and is included as part of the calibration (2003 NELAC regulation 5.5.5.2.2.1.h.3). The PQL is determined by running ten replicate samples with a concentration that will produce a recovery of 70-130% for most analytes, but the recovery requirements are analyte dependent. The PQL is referred to as the Method Reporting Limit (MRL) in LIMS.

18.3 Current LODs and PQLs are stored at: General and Admin\Quality Assurance\MDLs & PQLs.

19) Quality Assurance/Quality Control:

19.1 Preventative maintenance –All maintenance must be documented in the instrument maintenance logbook. Correct instrument optimization is a crucial part of the quality control.

19.2 The instrument performance check must meet the requirements.

19.3 The correlation coefficients of calibration curves (R) for each element must be ≥ 0.995 on at least five standards to proceed with sample analysis. If the correlation coefficients for any element do not meet the requirement, results for that element must not be reported from that run.

19.3.1 When analyzing samples by EPA 1638 or 200.8, the recovery of all calibration points must be between 50% and 150%. When analyzing samples by EPA 6020B, the recovery of the top two calibration points must be between 90% and 110% and all other calibration points must recover between 80% and 120%.

19.3.2 The concentration axis intercept shall be below the PQL.

19.3.3 If a sample concentration exceeds that of the highest calibration standard, the sample must be "E" flagged and diluted so that it is within the calibrated concentration range and any sample following the exceedance must be reanalyzed for confirmation with an "E-01" flag. If the sample is non-detect, no further action is necessary.

19.3 The ICV must be analyzed following the calibration. The CCV must be analyzed per 10 samples.

19.4 The ICB and CCBs shall be monitored for the effects of carry-over. The ICB must be analyzed following the ICV. The CCB must be analyzed following the CCV and must be analyzed per 10 samples. An analytical sequence will end with the analysis of a CCV/CCB pair. The **absolute value** of analyte concentrations in the ICB/CCB must be less than the PQL for methods 1638 and 200.8. The **absolute value** of analyte concentrations in the ICB/CCB must be less than 1/2 the PQL for method 6020B.

19.5 Each digestion batch (or analytical batch for the analysis of dissolved elements) must have at least one associated preparation blank and Eurofins Seattle suggests one preparation blank per 10 samples. These are treated exactly the same as the samples, and must go through all of the same preparative steps. The **absolute value** of analyte concentrations in the preparation blank must be less than the PQL for methods 1638 and 200.8. The **absolute value** of analyte concentrations in the preparation blank must be less than 1/2 the PQL for method 6020B.

19.6 For certain clients, the absolute value of analyte concentrations in preparation blanks and ICB/CCBs must be below the MDL (e.g. State of Louisiana). Project managers will communicate these requirements to the laboratory via method or login comments in the LIMS.

19.7 One or more rinse blanks, comprised of only dilute acid, must be run after any samples suspected to be high in metals content. Each rinse is to be treated as a discrete injection

19.8 A matrix duplicate (MD) sample analysis may be performed at the request of a client. Depending on client-specified preferences, the MD shall be client-specific or batched between two or more clients. The relative percent difference (RPD) for the replicates must be ≤20% if the sample concentrations are greater than 10 times the PQL. A duplicate matrix spike (MSD) shall be substituted for the MD, with the same control limit applying.

19.9 For each set of 10 or less samples, a matrix spike (MS) and a matrix spike duplicate (MSD) analysis shall be performed. Depending on client-specified preferences, the MS and MSD shall be client-specific or batched between two or more clients.

19.10 For each set of 20 samples, an LCS/LCSD (or OPR duplicate) analysis shall be performed.

19.11 If analyzing samples by EPA 6020B, the concentration of target analytes in the ICSA must be less than 2 times the reporting limit. Additionally, the recovery of target analytes spiked in the ICSAB must fall between 80% and 120%.

19.12 For each batch analyzed by EPA 6020B, one post-digestion spike (PDS) and dilution test (SD) must be performed. The PDS digestion spike is performed by spiking an aliquot of a sample from the batch at approximately the mid-point of the calibration. The dilution test is performed by analyzing a sample at a dilution 5 times greater than the primary reportable result.

19.13 As internal standardization is used for quantitation in this procedure, an element not present in client samples must be selected as an internal standard for each target analyte. The mass of this internal standard should be within 50 amu of the target analyte mass. Internal standard recoveries for all reported results must be between 30% and 150%.

20) Corrective Action

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20.1 The Quality Control data obtained during the analyses provide an indication of the quality of the sample data. The QC limits are defined in the QC section and determine if the preparation batch must be reanalyzed.

20.2 Corrective action is required if quality assurance parameters are out, or if the analyst believes it is necessary. First, a careful re-evaluation of the calculations involved must be done.

20.3 Corrective action will then be carried out as decided by the Trace Metals Laboratory Manager and QC Manager. Some data can be qualified, but must be left up to Laboratory Manager/QA Manager for final approval.

20.4 If an internal standard continues to fail, performing a post spike on the sample will determine if the matrix is causing suppression or enhancement. If the post spike is in control and the internal standard fails the data can be qualified. If both the post spike and the internal standard fail an alternate dilution with post spike should be analyzed.

20.5 The Quarterly Check Standard: Determine the mean concentration from three analyses, the check standard must be within ± 10% of the stated QCS value and is performed on a quarterly basis. If the check standard is not within the required limits, an immediate second analysis of the check standard is recommended to confirm unacceptable performance. If the check standard continues to fail and calibration standards and/or acceptable instrument performance cannot be verified, the source of the problem must be identified and corrected before proceeding with further analyses for that metal.

21) List of Attachments

Table 1: Example of an Analytical Sequence for 1638/200.8
Appendix A: Analysis of Non-Routine Metals
Appendix B: Troubleshooting Tips

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Table 1:
Example of an Analytical Sequence for 1638/200.8

SOP5135	EPA 1638
ICV-SDS	**ICV-PDS**
ICB	ICB
OPR1-SDS (BS1)	**OPR1-SDS**
OPR2-SDS (BSD1)	MB1
MB1	Sample #1
MB2	Sample #2
Sample#10	Sample #3
MS1	Sample #4
MSD1	Sample #5
Sample#20	Sample #6
MS2	Sample #7
MSD2	Sample #8
CCV1-SDS	CCV1-PDS
CCB1	CCB1
Sample #1	Sample #9
Sample#2	Sample#10
Sample#3	MS1
Sample#4	MSD1
Sample#5	**OPR2-SDS**
Sample#6	MB2
Sample #7	Sample #11
Sample #8	Sample #12
Sample #9	Sample #13
Sample #11	Sample #14
CCV2-SDS	CCV2-PDS
CCB2	CCB2
Sample #12	Sample #15
Sample #13	Sample #16
Sample #14	Sample #17
Sample #15	Sample #18
Sample #16	Sample #19
Sample#17	Sample#20
Sample #18	MS2
Sample#19	MSD2
CCV3-SDS	CCV3-PDS
CCB3	CCB3

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Appendix A: Analysis of Non-Routine Metals

1. Non-routine elements such as, but not limited to Bi/In/Rh/Ir/Rb/Ru/W/Pd/Pt/Os/Th/La/Li7/Au, are generally never present in the calibration standards.

1.1. A non-routine metal is laboratory defined as any metal outside of the SM-1411-006 custom spikes.

1.2 Other metals can be added to the non-routine list based on laboratory research, standard availability and metal compatibilities.

1.3 Prior to any receipt of non-routine metal analysis, the Laboratory Manger must be notified for standard availability and instrument capabilities.

1.3.1 Special care must be taken when preparing these standards for incompatibilities as well as whether the element of interest is used as an internal standard for routine analysis. If the metal requested is used as an internal standard such as Bi, In or Rh, the instrument must be pre-cleaned to remove residual trace of these elements.

1.3.2 Once it has been established that standards are available, internal standard overlaps and compatibilities are evaluated, the instrumentation must be verified that the appropriate optimization files are being utilized for analysis.

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APPENDIX B: Troubleshooting Tips

1. Plasma shut down or will not ignite:
   - **1.1.** Check Torch alignment.
   - **1.2.** Spray chamber may not be draining properly.
   - **1.3.** Possible air leak, verify that the Argon connections and Auxiliary connections are secure on the torch.
   - **1.4.** Verify that the torch is not cracked.
   - **1.5.** Verify that torch box temperature is not overheating.
2. Vacuum pressure
   - **2.1.** Verify that cones are seated properly.
   - **2.2.** If vacuum pressure drops during analysis, the sample cones may be clogged.
3. Low Sensitivity
   - **3.1.** Verify that standards we prepared properly.
   - **3.2.** Worn sample line tubing.
   - **3.3.** Torch alignment may need adjusting.
   - **3.4.** Cones, tubing, or injector may have clog.
   - **3.5.** Rotor may need cleaning or replacement.
4. High RSDs
   - **4.1.** Nebulizer partially clogged.
   - **4.2.** Improper tension on the peristaltic tubing.
   - **4.3.** Possible carryover, if previous sample contained elevated levels of the metal in question.
   - **4.4.** Probe is aspirating air.
5. High Oxides
   - **5.1.** Nebulizer gas flow to high.
   - **5.2.** Dirty cones.
6. High Doubly Charged

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6.1. Contaminated solution.

6.2. Verify that cones are seated properly.

7. High Background

7.1. High running pressure. This is normal if the system has recently been opened. Allow the vacuum to return to normal vacuum pressure.

7.2. If lens was recently replaced, was the autolens cleaned prior to installation with 1-3% HNO_3.

7.3. Detector may be going out. Consult with the Laboratory Manager.

8. See L:\Nutra General Files\Instrument Manuals\Agilent ICP-QQQ\Troubleshooting for more information on troubleshooting.

EFGS-P-SP-SOP2798 Ultra-Clean Sample Filtration
EFGS-Q-QM-QM5805 Quality Assurance Manual
EFGS-S-CS-SOP2794 Ultra-Clean Aqueous Sample Collection
EFGS-S-HS-QP12066.0004 Chemical Hygiene Plan
EFGS-S-HS-SOP2991 Waste Disposal Procedures for Client Sample Waste
EFGS-S-HS-SOP5670 Health and Safety Evaluation and Auditing
EFGS-S-IT-WI7061 Eurofins Frontier Global Sciences - Instrument and Instrument Software Inventory
EFGS-S-SB-SOP5139 Cleaning of Sampling Equipment and Bottles for Trace Metals Analysis
EFGS-T-TM-SOP2821 HF/HNO3/HCl Microwave Digestion of Solids Followed by Repeated HNO3 Evaporation for Trace Metals
EFGS-T-TM-SOP2825 Total Recoverable Metals in Solids Using a Nitric Acid Oven Bomb Digestion
EFGS-T-TM-SOP2836 Digestion for Total Recoverable Metals in Waters by Oven Heating
EFGS-T-TM-SOP2837 Total Recoverable Metals Digestion for Solid, Animal or Plant Materials
EFGS-T-TM-SOP5145 Total Recoverable Metals in Solids via Microwave Digestion
EFQA-Q-QD-SOP2711 Pipette and Dispenser: Operation, Calibration & Maintenance
EFTM-T-TM-SOP2820 Reductive Precipitation
EFTM-T-TM-SOP2840 Total Recoverable Metals in Sediments and Soils via a Modified Aqua Regia Oven Bomb Digestion
EFTM-T-TM-SOP2988 Extraction of Trace Metals from Seawater by Co-APDC

End of document

Version history

Version	Approval	Revision information	
14	04.MAR.2019		
15	10.SEP.2021		
16	31.JUL.2024		

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eurofins	Always check on-line for validity. **Digestion for Total Recoverable Metals in Waters by Oven Heating**	Level: **Standard Operating Procedure**
Document number: **EFGS-T-TM-SOP2836**		
Old Reference: **FGS-052**		
Version: **14**		Organisation level: **4-Business Unit**
Approved by: **GR8L, GW2R** Effective Date: **18-MAR-2024**	Document users: **EFGS_TraceMetal**	Responsible: **EFGS_SMM**

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DOCUMENT IS NOT CONTROLLED WHEN PRINTED

1) Revision Log:
2) Reference:
3) Cross Reference:
4) Purpose:
5) Scope:
6) Basic Principles:
7) Reference Modifications:
8) Definitions:
9) Interferences:
10) Safety Precautions, Pollution Prevention and Waste Handling:
11) Personnel Training and Qualifications:
12) Sample Collection, Preservation, and Handling:
13) Apparatus and Equipment:
14) Reagents and Standards:
15) Calibration:
16) Procedure:
17) Calculations:
18) Statistical Information/Method Performance:
19) Quality Assurance/Quality Control:
20) Corrective Action

1) Revision Log:

Revision: 14	**Effective Date:**	This version
Section	**Justification**	**Changes**
Throughout	Required	Updated laboratory name to Eurofins Seattle
Throughout	Required	Removed aqueous ceutical sample procedures and language
5	Required	Removed section 5.2 and updated section names
5.1	Required	Removed hydrofluoric digestion
5.2	Required	Removed HG-AFS analysis
6	Required	Updated digestion time; Removed 6.2.1.1
8	Required	Updated MBLK and BLK to MB
9	Required	Removed section 9.2 and updated section names
10	Required	Removed section 10.4 and updated section names
13.1	Required	Updated LIMS system
13.2.4	Required	Removed section
13.6	Required	Removed to reflect new logbook practice
14.3.1	Required	Removed, redundant
14.5	Required	Removed section

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Revision: 14	**Effective Date:**	This version
16	Required	Updated to match new LIMS and logbook practice
16	Required	Removed section 16.5 and updated section names
16	Required	Removed total metals procedure information
16.4.2	Required	Changed BLK to MB and BS to LCS
16.6	Required	Removed sections 16.6.1 and 16.1.1 with alternate digestion times; adjusted digestion time
16.7.1	Required	Added procedure for filtering samples
18.2	Required	Edited PQL definition
18.3	Required	Updated storage location for limits
19	Required	Added spiking volumes for QC

Revision: 13	**Effective Date:**	09/10/2021
Section	**Justification**	**Changes**
2.6	Required	updated reference
3	Required	Added CHP
14.3.1	Required	Added pipette rinse

2) Reference:

2.1 Chemical Hygiene Plan, Eurofins Seattle, current version.

2.2 Bloom, N.S, and Gauthier, M.L. 1998. "Lower MDLs and Better Accuracy for 'Total Recoverable Metals' in Water through the Use of Dilute HF/HNO3.

2.3 Method 200.8, "Determination of trace elements in waters and wastes by inductively coupled Plasma-Mass Spectrometry," revision 5.4.

2.4 Method 1638 "Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma — Mass Spectrometry," January 1996.

2.5 TNI Environmental Laboratory Sector, Vol 1, Management and Technical Requirements, ELV1-2016.

2.6 Department of Defense / Department of Energy Consolidated Quality Systems Manual for Environmental Laboratories, prepared by DoD Environmental Data Quality Workgroup (EDQW) and DOE Consolidate Audit Program (DOECAP) Data Quality Workgroup (DOE-DQW), Version 5.3, May 2019.

2.7 AOAC Official Method 993.14 Trace Elements in Waters and Wastewaters Inductively Coupled Plasma–Mass Spectrometric Method First Action 1993.

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3) Cross Reference:

Document	Document Title
EFGS-Q-QM-QM5805	Quality Manual
EFGS-S-HS-12066	Chemical Hygiene Plan
EFGS-Q-QD-SOP41510	Volumetric Verification and Pipette and Dispenser Operation and Maintenance
EFGS-T-TM-SOP5135	Determination of Trace Metals by ICPMS
EFGS-S-SB-SOP5139	Cleaning of Sampling Equipment and Bottles for Trace Metals Analysis
EFGS-S-HS-SOP2991	Waste Disposal Procedure for Client Sample Waste
EFGS-S-HS-SOP5670	Health and Safety Evaluation and Auditing

4) Purpose:

4.1 The purpose of this standard operating procedure is to describe the oven digestion procedure used for water samples at Eurofins Seattle prior to the analysis of total recoverable metals.

5) Scope:

5.1 Environmental waters: This method is a closed-vessel, oven-heated digestion procedure of water for analysis of total recoverable (2%/0.5% nitric/hydrochloric acid digestion) metals.

5.2 Sample analysis is performed by inductively coupled plasma-mass spectrometry (ICP-MS).

6) Basic Principles:

6.1 Samples are acid preserved to a pH <2 with nitric acid.

6.2 Samples are heated in an oven at 85±5°C for three hours.

6.2.1 Add additional hydrochloric acid 0.5% (v/v) and nitric acid 1% (v/v) prior to digestion.

6.3 When removing the 50 mL centrifuge vials used for total recoverable digestion, ensure that the caps are tight to prevent evaporation of sample and invert samples.

6.4 Once cool, place samples on the "to be" analyzed shelf.

6.5 Aliquots are to be taken from the supernatant of the sample for analyses. DO NOT shake samples prior to analysis.

6.6 Acidification will not be performed only at the request of a project manager or Trace Metals Leads for special projects.

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7) Reference Modifications:

7.1 In section 16.4.2.1, the addition of individual acids HNO3 and HCl for 200.8/1638 were replaced with a combined HNO3-HCl acid solution, keeping the proportions the same.

8) Definitions:

8.1 Batch – no more than 20 client samples grouped for preparation. 1 Preparation Blank per 10 samples, 1 CRM or 1 LCS/LCSD per 20 samples; 1 MS/MSD set is prepared for every 10 samples.

8.2 Celsius (C), conversion of Celsius to Fahrenheit: (C * 1.8) + 32

8.3 Fahrenheit (F), conversion of Fahrenheit to Celsius: (F - 32) / 1.8

8.4 Method Detection Limit (MDL) – the limit derived from an exercise as described in 40 CFR, Part 136, Appendix B. The exercise produces a defined value that is the minimum concentration that can be measured and reported with 99% confidence that the analyte concentration is greater than zero from a given matrix.

8.5 Practical Quantitation Limit (PQL) – the minimum concentration that can be reported quantitatively. The PQL is the upper Control Limit for the absolute value of the individual ICB, CCB, and MB; i.e. the instrumental value of these QC standards must be lower in concentration than PQL. In the LIMS, the PQL is referred to as the reporting limit (RL).

8.6 Limit of Detection (LOD) – The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%. The LOD shall be at least 2 times but no greater than 4 times the DL for multiple analyte methods or 2 times but no greater than 3 times the DL for single analyte methods.

8.7 Limit of Quantitation (LOQ) – equal to PQL and verified on an annual basis by spiking at or below the LOQ.

8.8 Certified Reference Material (CRM) – a standard of known composition that is certified by a recognized authority and representing a sample matrix. It is used to verify the accuracy of a method.

8.9 Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD), is a sample containing known concentrations of the analytes of interest that is taken through the entire preparation and analysis process in the same manner as the samples to monitor complete method performance. A Certified Reference Material (CRM) is preferred as the LCS, but a blank spiked sample also meets the requirement.

8.10 LIMS – Laboratory Information Management System

8.11 Method Blank (MB) – Method blanks consist of the same reagents used to digest the samples, in the same volume or proportion, and are carried through the complete sample preparation and analytical procedure. Teflon boiling chips are used in absence of a matrix.

8.12 Matrix Duplicate (MD) – a representative sample is selected and digested in the same manner. This QC sample will indicate sample homogeneity on the analytes of interest and is prepared at the client request.

8.13 Matrix Spike (MS) and Matrix Spike Duplicate (MSD) – a representative sample is selected and spiked at the same levels as a Blank Spike. These QC samples will indicate sample matrix effects on the analytes of interest.

8.14 May: This action, activity or procedure is optional.

8.15 May Not: This action, activity or procedure is prohibited.

8.16 Shall: This action, activity or procedure is required.

8.17 Should: This action, activity or procedure is suggested, but is not required.

9) Interferences:

9.1 Centrifuge tubes; if not capped tightly, the sample can evaporate, causing the analyte concentrations to be bias high or bias low depending on the volatility of the element.

9.2 Due to the relative high concentration of hydrochloric acid (HCl) in this digestate, analysis by inductively coupled plasma – mass spectrometry (ICP-MS) is not ideal for metals such as Cr, V, Mn, Cu, As, and Se without the use of either collision cell (KED) or dynamic reaction cell (DRC) modes on the ICP-MS.

9.3 Due to the presence of gold in this digestate, analysis by inductively coupled plasma – mass spectrometry (ICP-MS) should be limited to designated instruments, whenever possible, to minimize the precipitation of silver in the analysis.

9.4 Particulates must be allowed to settle out of solution; otherwise, they could clog the ICP-MS sample introduction system.

10) Safety Precautions, Pollution Prevention and Waste Handling:

10.1 Personnel will don appropriate laboratory attire according to the Chemical Hygiene Plan (CHP) *EFGS-S-HS-12066*. This includes, but is not limited to, laboratory coat, eye protection and protective gloves.

10.2 The toxicity or carcinogenicity of reagents used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Chemists should refer to the SDS (Safety Data Sheets) for each chemical they are working with by referring to the SDS located at: https://msdsmanagement.msdsonline.com/company/5c1df5b3-747d-4789-8104-42457dc3a3e5/.

10.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease-causative agents.

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Eurofins Seattle will reimburse the expense of Hepatitis A and B immunizations for any laboratory staff member who desires this protection.

10.4 Hydrochloric acid: Very hazardous in case of skin contact (corrosive, irritant, permeator), of eye contact (irritant, corrosive), of ingestion. Slightly hazardous in case of inhalation (lung sensitizer). Non-corrosive for lungs. Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. Severe over-exposure can result in death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

10.4.1 Eye Contact:

10.5.1.1 Check for and remove any contact lenses (contact lenses shall never be worn in the laboratory). In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention immediately.

10.4.2 Skin Contact:

10.5.2.1 In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Cover the irritated skin with an emollient. Cold water may be used. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention immediately.

11) Personnel Training and Qualifications:

11.1 All technical staff must have read this SOP, been trained by experienced personnel and have the training documents on the applicable form(s) before performing this procedure**.**

11.2 An analyst must perform an initial demonstration of capability (IDOC) that includes four replicates of a secondary source before being qualified to analyze samples without supervision. Continuing DOC will be maintained and monitored via performance on QC samples and CRMs, as well as obtaining acceptable results on proficiency testing exercises.

11.3 The analyst/laboratory technician must have read this SOP and other relevant SOPs and have the training documented on the applicable form(s). The analyst may be questioned on SOP by supervisor(s) and/or trainers.

11.4 Training is documented by the employee and supervisor, and is kept on file in the QA Office. The employee must read, understand, and by signing the training document, agree to perform the procedures as stated in all Standard Operating Procedures (SOPs) related to this method.

11.5 All employees must read the Quality Manual (QM) (*EFGS-Q-QM-QM5805*) and complete annual Ethics training.

11.6 All training documents including IDOCs, CDOCs, Initial QA orientation, and Ethics training are stored by the Quality Assurance Manager in the employees training file for ten years after the employee is no longer working for Eurofins Seattle.

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11.7 Chemical Safety Training, Compressed Gas Training, Chemical Hygiene Plan documentation, and Shipping of Hazardous goods, are stored by the Health and Safety Officer for ten years after the employee is no longer working for Eurofins Seattle.

12) Sample Collection, Preservation, and Handling:

12.1 Client samples are preferably collected in PETG bottles provided by Eurofins Seattle. These bottles are new 250 mL, 500 mL, or 1000 mL and purchased from Fisher Scientific or equivalent and cleaned according to SOP *EFGS-S-SB-SOP5139* prior to being sent to clients.

12.1.1 Water samples are often sent in the client sample container and not in bottles supplied by Eurofins Seattle. No bottle blanks can then be created.

12.2 Samples are preserved to *a* pH of <2 with nitric acid at the time of receipt.

12.3 Acidification will not be performed only at the request of the project managers or Trace Metals Leads for special projects.

13) Apparatus and Equipment:

13.1 LIMS – TALS (current production version); Computer – Windows 10

13.2 Digestion Bottles for 1% nitric digestion: 50 mL Digestion vessels (CLASS-A) from SCP Science, or equivalent, with white digestion caps, or Centrifuge Tubes from CPI International or equivalent that have been volume tested at 50 mL size and have been cleaned according to SOP *EFGS-S-SB-SOP5139* are used for common contaminant metals. If a volume tested tube is used, volume testing must be verified for the lot number used and must be submitted for review.

13.2.1 SCP Class A tubes are to be used when the client is requesting all metals excluding Zinc.

13.2.2 CPI tubes are to be used when the client is requesting all metals excluding Aluminum.

13.2.3 If a client requests both Al/Zn, the SCP Class A tubes should be used for the initial digestion.

13.3 Drying Oven: Stainless steel laboratory oven, capable of maintaining 85°C±5°C

13.4 Clean-Air Station: Class-100 particulate-free clean air station (HEPA filter).

13.5 Pipettors: All-plastic, pneumatic, fixed volume and variable pipettes in the range of 5 µL to 10 mL. Pipettes are to be calibrated weekly according to SOP *EFGS-Q-QD-SOP41510*.

14) Reagents and Standards:

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14.1 Reagent Water: 18 MO ultra-pure deionized water starting from a pre-purified (distilled, R.O., etc.) source. As a final mercury and organic removal step, the activated carbon cartridge on the 18-MO system is placed between the final ion exchange bed and the 0.2 µm filter.

14.2 Hydrochloric Acid (HCl): Concentrated (36.5%-38.0% weight basis) low trace-metals grade hydrochloric acid. Several brands (Baker, Fisher, Omnitrace) have been found to have lots with acceptably low levels of trace metals. This reagent must be from a lot number that has been previously tested to be low for the analytes of interest. This reagent shall be entered into LIMS and the expiration date is set to 3 years after receipt date.

14.3 Nitric Acid (HNO3): Concentrated (69%-70% weight basis) low trace-metal grade nitric acid. Several brands (Baker, Fisher, Omnitrace) have been found to have lots with acceptably low levels of trace metals. This reagent should be from a lot number that has been previously tested to be low for the analytes of interest. This reagent shall be entered into LIMS and the expiration date is set to 3 years after receipt date.

14.4 HNO3 Pipette Tip Rinse Solution, ~5% (v/v): Add 50 mL of concentrated HNO3 to 950 mL of reagent water. Volume can be modified based on the volume needed for the day.

15) Calibration:

15.1 There are no requirements for calibration or standardization for daily use.

15.2 The oven is monitored prior to the start of sample digestion. The oven must fall within the ranges specified in the SOP.

16) Procedure:

16.1 All samples received for total recoverable metal determination; samples are preserved to a pH <2 with nitric acid at a clean bench, wearing clean gloves, and using ultra-clean sample handling techniques and are stored at ambient temperature for 16 hours. Rinse pipette tips with rinse solution (~1-5% HNO3) before using.

16.1.1 Non-Acidified samples for total recoverable metals are prepared at a clean bench, wearing clean gloves, and using ultra-clean sample handling techniques. MQ will be used to rinse pipettes and as the sample diluents during analysis. The samples will be digested in MQ-rinsed only SCP tubes.

16.1.2 The pH value is recorded in LIMS prior to aliquoting the client sample.

16.1.3 If for some reason, such as high alkalinity, the sample pH is verified to be >2, more acid must be added and the sample held for 16 hours until the pH is verified to be <2. The sample pH is documented in the preservation logbook.

16.1.4 The sample is re-logged into the preservation logbook and the preservation sheet with the amount of additional acid added is recorded in LIMS.

16.2 For samples requiring EPA Method 200.8; following acidification the sample should be mixed, held for 16 hours at ambient temperature, and then verified to be pH <2 just prior

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withdrawing an aliquot to be oven digested or for "direct analysis," for dissolved samples. Rinse pipette tips with rinse solution (~1-5% HNO3) before using.

16.2.1 The pH value is recorded in LIMS prior to aliquoting the client sample.

16.2.2 If for some reason, such as high alkalinity, the sample pH is verified to be >2, more acid must be added and the sample held for 16 hours until the pH is verified to be <2. The sample pH is documented in the preservation logbook.

16.2.3 The sample is re-logged into the preservation logbook and the preservation sheet with the amount of additional acid added is recorded in LIMS.

16.2.4 200.8 and 1638 samples can be digested within the same batch as long as the preservation times are met as per the SOP.

16.3 For samples requiring EPA Method 1638; Store the preserved sample for a minimum of 48 hours at 0-4°C to allow the acid to completely dissolve the metal(s) adsorbed on the container walls. The sample pH should be verified as <2 immediately before withdrawing an aliquot for processing or direct analysis. Rinse pipette tips with rinse solution (~1-5% HNO3) before using.

16.3.1 The pH value is recorded in LIMS prior to aliquoting the client sample.

16.3.2 If, for some reason such as high alkalinity, the sample pH is verified to be >2, more acid must be added and the sample held for 16 hours until verified to be pH <2. The sample pH is documented in the preservation logbook.

16.3.3 The sample is re-logged in to the preservation logbook and the preservation sheet with the amount of additional acid added is recorded in LIMS.

16.3.4 1638 and 200.8 samples can be digested within the same batch as long as the preservation times are met as per the SOP.

16.4 Samples for total recoverable analysis are split into 50 mL centrifuge vials. Homogenize samples by inverting several times. Pour the aliquot into the corresponding labeled centrifuge tube.

16.4.1 Sample preparation for dissolved metals only: An aliquot is split into a 50mL centrifuge tube and further preserved to a 1% (v/v) with HNO3. Cap and invert sample. The sample is ready for analysis. If a client is requesting both Total Recoverable and Dissolved analysis, prepare the dissolved samples as seen in Section 16.4.3 alongside the total recoverable fractions. Note: if a precipitate is formed prior to preservation or after the initial preservation, the sample must be treated using Section 16.4.3.

16.4.2 Total Recoverable Water Digestion: Further preservation in the 50mL tube to 1% (v/v) with HNO3 and 0.5% (v/v) with HCl is performed if a complete sample digestion is not desired. However, this method leaches metals off of the surface of the particles rather than dissolving the particles, and it will result in a lower recovery for some analytes. This "total recoverable" digestion is a modified version of many EPA methods (EPA 1638 and 200.8).

16.4.2.1 For 1638/200.8, after all samples including MBs and LCS/LCSDs are at a pH <2, and all of the QC have all been appropriately identified/spiked, the following must be completed:

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- Prepare a 2:1 HNO3/HCl solution in a rinsed 50 mL centrifuge tube, with an expiration date of 1 day.
- 2:1 HNO3/HCl - 30mL HNO3 and 15mL HCl.
- To minimize waste, only prepare the volume required for the batch. **Prepare per batch.**
- It is critical that this be prepared less than 10 minutes prior to reagent addition as to avoid the generation of aqua regia.
- To each centrifuge tube, add 0.750 mL of the 2:1 HNO3/HCl solution per 50mL of sample using a calibrated pipette.
- If this step has been started, it must be completed. Avoid distractions.
- It is important to note, that the longer this solution sits, the less efficacy it has.

16.4.2.2 1638 and 200.8 samples can be digested within the same batch as long as the preservation times are met as per the SOP.

16.4.3 Preservation to 1% (v/v) with HCl may be sometimes requested by the client for specific analyses.

16.5 Cap all sample containers tightly. Put centrifuge tubes in a rack on a glass tray and place in an oven preheated to 85±5°C. Document the following items: Record the initial/final oven temperatures and start/end times of the digestion in LIMS. Ensure that the oven is set appropriately so that the temperature does not exceed 85±5°C. A higher temperature may cause loss of sample. Heat the samples in the oven for 3 hours.

16.6 Upon removing the samples from the oven, ensure that the caps to the centrifuge vials, are still on tight to prevent evaporation (under a fume hood if possible). Invert samples and release pressure from the samples. Repeat this step until all pressure has been released.

16.7 Once samples have reached room temperature, the digests are ready for analysis. Take the sample aliquot for analysis from the supernatant of the samples.

16.7.1 If sample filtration is required due to heavy particulate (a rare occurrence for water samples), method blanks and laboratory control samples must be filtered as well.

16.8 Instrument Maintenance and Troubleshooting

16.8.1 The oven is verified to be functioning correctly each day through the use of calibrated thermometers.

16.8.2 If the oven is found to not be able to maintain the appropriate temperature range on the date of analysis, the analyst will notify their supervisor and QA immediately and mark the oven as non-functioning and to not use. An external repair group will be called out to correct any problems with the oven and it will be verified to be functioning correctly through the use of calibrated thermometers prior to resuming digestions in the oven.

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17) Calculations:

17.1 This preparation procedure does not involve calculations.

18) Statistical Information/Method Performance:

18.1 Method Detections Limits (MDL) are determined during method development and then annually thereafter according to 40 CFR Part 136, Section B and CA-Q-S-006.

18.2 The Practical Quantitation Limit (PQL) is the reporting limit for this method and is included as one of the calibration points.

18.3 Current LODs and PQLs are stored at in the LIMS.

19) Quality Assurance/Quality Control:

19.1 For analysis according to *EFGS-T-TM-SOP5135* "Determination of Trace Elements by Inductively Coupled Plasma-Mass Spectrometry (Adapted from EPA Method 1638 for water samples)," one method blank will be prepared for every set of 10 samples.

19.1.1 Centrifuge tubes are filled with reagent water and preserved in the same manner as the samples in the batch. An additional filter blank may be included if the samples were filtered for dissolved metals in the batch.

19.2 For analysis according to *EFGS-T-TM-SOP5135* "Determination of Trace Elements by Inductively Coupled Plasma-Mass Spectrometry (Adapted from EPA Method 1638 for water samples)," for every set of 10 samples 1 set of MS/MSD are digested with the samples. For every set of 20 client samples a set of LCS/LCSD (OPR1/2) are to be digested.

19.2.1 The LCS/LCSD is prepared by spiking a method blank with 25µL of the prep spike standard in *EFGS-T-TM-SOP5135* per 50mL of solution.

19.2.2 The MS and MSD are prepared by spiking a representative sample (known field blanks or equipment blanks should not be used) with analyte at mid-level. The spike must be well-mixed with the sample. After all the QC samples are prepared, they are digested by the same analytical process as the samples.

19.2.2.1 The selection of the MS/MSD sample selection is random. If a known field blank or equipment blank is chosen, notify Trace Metals Laboratory Manager, Quality Assurance Officer and Project Manager.

19.2.2.2 The MS/MSD is to be spiked with 25µL of the prep spike standard in *EFGS-T-TM-SOP5135* per 50mL of solution.

19.2.3 Spiking Witness: This is required for all digests. The spike witness must verify that the appropriate samples are being spiked prior to spike addition. A valid spike witness must have a valid DOC for a minimum of 6 months.

20) Corrective Action

20.1 If the pH is above 2 when measured after a minimum of sixteen hours (for EPA 200.8), this must be noted in the pH logbook and a comment should be entered to the MMO notes and the project manager must be notified.

20.2 If the pH is above 2 when measured after a minimum of 48 hours (for EPA 1638), this must be noted in the pH logbook and a comment should be entered to the MMO notes and the project manager must be notified.

20.3 If the sample was not stored at a temperature 0-4°C for 48 hours (for EPA 1638) the Quality Manager must be notified.

20.4 If the oven temperature exceeds 85±5°C, inspect the samples for any obvious volume loss. If any sample has obviously evaporated, or if there is any question regarding volume loss, consult with the Trace Metals Laboratory Manager and/or the Quality Assurance Manager and notify the Project Manager. Write appropriate notes in the MMO notes in LIMS. Analysis should not be attempted on these samples, unless directed to do so by the Trace Metals Laboratory Manager and/or the Quality Assurance Manager. Inspect oven to make sure that all settings were correct. If oven settings were correct, discontinue using the oven and notify the Quality Assurance Manager. An incident report should be generated and an internal investigation of the ovens temperature settings should be performed. The oven should be scheduled for calibration by an external company and service if needed.

20.5 In the event that the method blanks are biased high for an analyte of interest, the blank is reanalyzed for confirmation. If the blank confirms the high bias and if the samples within the batch cannot be qualified, the samples are to be re-digested.

20.6 In the event that the LCS/LCSD are biased high for an analyte of interest, the LCS/LCSD is reanalyzed for confirmation. If the LCS/LCSD confirms the high bias and if the samples within the batch cannot be qualified, the samples are to be re-digested.

20.7 In the event that the LCS/LCSD are biased low for an analyte of interest, all samples are to be re-digested.

EFGS-Q-QD-SOP41510 Volumetric Verification and Pipette and Dispenser Operation & Maintenance
EFGS-Q-QM-QM5805 Quality Assurance Manual
EFGS-S-HS-QP12066.0004 Chemical Hygiene Plan
EFGS-S-HS-SOP2991 Waste Disposal Procedures for Client Sample Waste
EFGS-S-HS-SOP5670 Health and Safety Evaluation and Auditing
EFGS-S-SB-SOP5139 Cleaning of Sampling Equipment and Bottles for Trace Metals Analysis
EFGS-T-TM-SOP5135 Determination of Trace Metals by ICPMS

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Version history

Version	Approval	Revision information	
12	15.AUG.2018		
13	10.SEP.2021		
14	18.MAR.2024		

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eurofins	Always check on-line for validity. **Distillation of Aqueous Samples for Methyl Mercury Analysis**	Level: **Standard Operating Procedure**
Document number: **EFGS-T-AFS-SOP2797**		
Old Reference: **EFGS-SOP-013**		
Version: **13**		Organisation level: **4-Business Unit**
Approved by: **GR8L** Effective Date: **23-JAN-2024**	Document users: **EFGS_TraceMetal**	Responsible: **EFGS_SMM**

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DOCUMENT IS NOT CONTROLLED WHEN PRINTED

1) Revision Log:
2) Reference:
3) Cross Reference:
4) Purpose:
5) Scope:
6) Basic Principles:
7) Reference Modifications:
8) Definitions:
9) Interferences:
10) Safety Precautions, Pollution Prevention and Waste Handling:
11) Personnel Training and Qualifications:
12) Sample Collection, Preservation, and Handling:
13) Apparatus and Equipment:
14) Reagents and Standards:
15) Procedure:
16) Calculations:
17) Statistical Information/Method Performance:
18) Quality Assurance/Quality Control:
19) Corrective Action:

1) Revision Log:

Revision: 13	**Effective Date:**	This version
Section	**Justification**	**Changes**
Throughout	Required	Changed company to Eurofins Seattle
Throughout	Required	Changed "Monomethyl mercury" to methylmercury
9	Required	Clarified language
12	Required	Corrected storage temperature requirement
13	Required	Updated equipment to new Tekran distillation apparatus
14	Required	Clarified language
15	Required	Updated procedure for use of Tekran 2750 distillation apparatus
17	Required	Removed limits and referenced LIMS
18	Required	Updated checklists to electronic versions

Revision: 12	**Effective Date:**	09-28-2021
Section	**Justification**	**Changes**
8	Required	Removed MD from batch definition/removed duplicate entries
13.3	Required	Removed MDN instructions
14.1.1	Required	Added pipette rinse
15.1.1, 15.4.1	Required	Removed MDN instructions
15.9	Required	Changed spike level to suggested vs set amount
18.4	Required	Removed requirement for MD

2) Reference:

2.1 Bloom, N.S. Determination of Picogram Levels of Methyl Mercury by Aqueous Phase Ethylation, Followed by Cryogenic Gas Chromatography with Cold Vapour Atomic Fluorescence Detection. Can. J.

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Fish. Aq. Sci. 1989, 46, 1131.

2.2 Bloom, N.S.; Fitzgerald, W.F. Determination of Volatile Mercury Species at the Picogram Level by Low-Temperature Gas Chromatography with Cold-Vapor Atomic Fluorescence Detection. Anal. Chem. Acta. 1988, 208, 151.

2.3 Horvat, M.; Bloom, N.S.; Liang, L. A Comparison of Distillation with Other Current Isolation Methods for the Determination of Methyl Mercury Compounds in Low Level Environmental Samples Part 2, Water. Anal. Chem. Acta. 1993, 282, 153.

2.4 Chemical Hygiene Plan, Eurofins Seattle, current version.

2.5 EPA Method 1630 Draft Method:, Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap and CVAFS, January 2001.

2.6 TNI Environmental Laboratory Sector, Vol 1, Management and Technical Requirements, ELV1-2016.

2.7 Department of Defense / Department of Energy Consolidated Quality Systems Manual for Environmental Laboratories, prepared by DoD Environmental Data Quality Workgroup (EDQW) and DOE Consolidate Audit Program (DOECAP) Data Quality Workgroup (DOE-DQW), Version 5.3, May 2019.

3) Cross Reference:

Document	Document Title
EFGS-Q-QM-QM5805	Quality Manual
EFGS-S-HS-12066	Chemical Hygiene Plan
CA-Q-S-006	Detection and Quantitation Limits
EFGS-Q-QD-SOP41510	Volumetric Verification and Pipette and Dispenser Operation and Maintenance
EFGS-S-CS-SOP2794	Ultra Clean Aqueous Sample Collection
EFGS-P-DR-SOP2801	Data Review and Validation and Monthly Logbook Review
EFGS-S-HS-SOP2991	Waste Disposal Procedure for Client Sample Waste
EFGS-T-AFS-SOP2808	Determination of Methyl Mercury in Various Matrices by Cold Vapor-Gas Chromatography- Atomic Fluorescence Spectrometry (EPA Method 1630)

4) Purpose:

4.1 The purpose of this Standard Operating Procedure (SOP) is to describe the method for the distillation of aqueous samples prior to analysis by CV-GC-AFS for methyl mercury.

5) Scope:

5.1 This method is for the distillation of aqueous samples (natural waters, precipitation, pore water, industrial and municipal effluents) for the analysis of methylmercury (MHg) at concentrations as low as 0.05 ng/L. In general, using clean handling and reagents, method detection limits (MDLs) in the range of 0.005 - 0.030 ng/L are routinely attainable.

5.2 Methyl mercury as defined by this method means all chloride-distillable methyl mercury forms and species found in aqueous solution and on aqueous suspended matter. This includes, but is not limited to, CH_3Hg^+, CH_3HgCl, CH_3HgOH, and CH_3HgS-R.

6) Basic Principles:

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6.1 Samples are collected using ultra-clean sample handling protocols into rigorously cleaned or tested clean glass bottles or disposable PETG bottles.

6.2 The samples must be acid-preserved within 48 hrs of sampling. Acid-preserved samples are stable for at least six months, if kept dark and cool (EPA 1630). Samples are preserved with 0.4% hydrochloric acid (HCl) and stored dark, in a refrigerator at a temperature between 0-4°C until distillation.

6.3 Before analysis, the MHg in an aliquot of the sample is co-distilled into pure water. The distillates are then analyzed for MHg by aqueous phase ethylation and Cold Vapor-Gas Chromatography-Atomic Fluorescence Spectroscopy (CV-GC-AFS) as described in SOP *EFGS-T-AFS-SOP2808* "Methyl Mercury Calibration and Analysis."

7) Reference Modifications:

7.1 No significant modifications were made to this method.

8) Definitions:

8.1 Batch – no more than 20 client samples grouped for preparation. 3 Preparation Blanks, 1 CRM or 1 LCS/LCSD (or BS/BSD) set per every 20 samples; 1 MS/MSD set is prepared for every 10 samples.

8.2 CDOC - Continuing Demonstration of Capability.

8.3 Certified Reference Material (CRM) – a standard of known composition that is certified by a recognized authority and representing a sample matrix. It is used to verify the accuracy of a method.

8.4 IDOC - Initial Demonstration of Capability.

8.5 Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD), reagent water is spiked with a secondary source at 1.0 ng/L and is taken through the entire preparation and analysis process in the same manner as the samples to monitor complete method performance. A Certified Reference Material (CRM) is preferred as the LCS, but a blank spiked sample also meets the requirement.

8.6 LIMS: Laboratory Information Management System. Computer software used for managing samples, standards, and other laboratory functions.

8.7 May: This action, activity or procedure is optional.

8.8 May Not: This action, activity or procedure is prohibited.

8.9 Method or Preparation Blank (BLK) – Method blanks consist of the same reagents used to digest the samples, in the same volume or proportion, and are carried through the complete sample preparation and analytical procedure.

8.10 Matrix Duplicate (MD) – a representative sample is selected and digested in the same manner. This QC sample will indicate sample homogeneity on the analytes of interest.

8.11 Matrix Spike (MS) and Matrix Spike Duplicate (MSD) – a representative sample is selected and spiked with a secondary source at 1.0 ng/L. These QC samples will indicate sample matrix effects on the analytes of interest.

8.12 Method Detection Limit (MDL) – the limit derived from an exercise as described in 40 CFR, Part 136, Appendix B. The exercise produces a defined value that is the minimum concentration that can be

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measured and reported with 99% confidence that the analyte concentration is greater than zero from a given matrix.

8.13 MHg - Methylmercury

8.14 Shall: This action, activity or procedure is required.

8.15 Should: This action, activity or procedure is suggested, but is not required.

9) Interferences:

9.1 The use of the distillation procedure eliminates most method interferences from organic matter, particulate, and sulfides, all of which can affect the recovery of methyl mercury.

9.2 Under no circumstances should ordinary plastic (i.e., polyethylene, polypropylene, polycarbonate, or vinyl) containers be used *with the exception of PETG containers*, as they are very diffusive to elemental mercury from the air. Containers should be made of acid-cleaned Teflon with Teflon caps, borosilicate (or quartz) glass bottles with Teflon-lined caps, *or PETG bottles*. It is critical that the bottles have very tightly sealing caps to avoid diffusion of atmospheric Hg through the threads.

9.3 The low detection limit of this method depends on the stringent cleaning of equipment used for sample collection and storage.

9.4 It is important that the HCl concentration in the sample be between 0.2% and 0.6% (v/v) for effective distillation of the CH3HgCl. If the chloride concentration present in the sample is too high (resulting from the addition of too much HCl upon preservation), HCl will co-distill with the sample during distillation, which lowers the pH of the distillate. If the low pH of the samples is not compensated for by adding additional acetate buffer, the sample will not be at the optimal pH for the ethylation reaction, resulting in slightly low recoveries. The problems associated with the distillation of samples high in chloride can also be avoided by distilling smaller aliquots of the sample; however, this results in higher detection limits. Typically, samples known to be high in chlorides (i.e., salinity) are preserved with 0.2% sulfuric acid. This minimizes the addition of chlorides to the sample, yet creates the appropriate sample pH for proper distillation.

9.5 No HNO3 or other oxidizing agents (i.e., Cl2, BrCl, CrO42-, etc.) can be present in the sample, or CH3Hg may be destroyed. Particular care must be taken to eliminate the chlorine present in the municipal water that feeds the deionized water system by passing it through an activated carbon bed.

10) Safety Precautions, Pollution Prevention and Waste Handling:

10.1 Personnel will don appropriate laboratory attire according to Chemical Hygiene Plan (CHP) *EFGS-S-HS-12066*. This may include, but is not limited to: laboratory coat, apron, eye protection, face shield and protective gloves.

10.2 The toxicity or carcinogenicity of each laboratory reagent has not been fully established. Therefore, every chemical must be treated as a potential health hazard. Exposures shall be reduced as much as possible. Analysts and technicians are expected to familiarize themselves with the characteristics and risks of each chemical they work with by referring to the SDS located at https://msdsmanagement.msdsonline.com/company/5c1df5b3-747d-4789-8104-42457dc3a3e5/

10.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease-causative agents. Eurofins Seattle will reimburse the expense of Hepatitis A and B immunizations for any laboratory staff member who desires this protection.

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10.4 Hydrochloric Acid (HCl) is hazardous. Always work in fume hood wearing safety glasses and gloves while using this chemical. In case of skin contact (corrosive, irritant, permeator), of eye contact (irritant, corrosive), of ingestion. Slightly hazardous in case of inhalation (lung sensitizer). Non-corrosive for lungs. Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. Severe over-exposure can result in death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

10.4.1 Eye Contact: Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention immediately.

10.4.2 Skin Contact: In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Cover the irritated skin with an emollient. Cold water may be used. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention immediately.

10.4.3 Serious Skin Contact: Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek immediate medical attention.

10.4.4 Inhalation: If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention immediately.

10.4.5 Serious Inhalation: Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. WARNING: It may be hazardous to the person providing aid to give mouth-to-mouth resuscitation when the inhaled material is toxic, infectious or corrosive. Seek immediate medical attention.

10.4.6 Ingestion: If swallowed, do not induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention immediately.

10.5 See Eurofins Seattle Chemical Hygiene Plan (CHP) for general information regarding employee safety, waste management, and pollution prevention.

10.6 Pollution prevention information can be found in the current EFGS Chemical Hygiene Plan (CHP), which details and tracks various waste streams and disposal procedures.

10.7 All laboratory waste is accumulated, managed, and disposed of in accordance with all federal, state, and local laws and regulations. Any waste generated by this procedure should be disposed of according to SOP *EFGS-S-HS-SOP2991* "Waste Disposal Procedure for Client Sample Waste," which provides instruction on dealing with laboratory and client waste.

11) Personnel Training and Qualifications:

11.1 An analyst must perform an initial demonstration of capability (IDOC) that includes four replicates of a secondary source before being qualified to analyze samples without supervision. Continuing DOC will be maintained and monitored via performance on CRMs and other QC samples, as well as obtaining acceptable results on proficiency testing exercises.

11.2 The analyst/laboratory technician must have read this SOP and other relevant SOPs and have the training documented on the applicable form(s). The analyst may be questioned on SOP by supervisor(s) and/or trainers.

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11.3 Training is documented by the employee and supervisor, and is kept on file in the QA Office. The employee must read, understand, and by signing the training document, agree to perform the procedures as stated in all Standard Operating Procedures (SOPs) related to this method.

11.4 All employees must read the Quality Manual (*EFGS-Q-QM-QM5805*) and complete annual Ethics training.

11.5 All training documents including IDOCs, CDOCs, SOP reading, Initial QA orientation, and Ethics training are stored by the Quality Assurance Manager in the employees training file for ten years after the employee is no longer working for Eurofins Seattle

11.6 Chemical Safety Training, Compressed Gas Training, Chemical Hygiene Plan documentation, and Shipping of Hazardous goods training, are stored by the Health and Safety Officer for ten years after the employee is no longer working for Eurofins Seattle.

12) Sample Collection, Preservation, and Handling:

12.1 Samples are collected using ultra-clean sample handling protocols into rigorously cleaned or tested clean glass bottles.

12.2 Aqueous sample preservation - The samples must be acid-preserved within 48 hrs of sampling. Samples are preserved with 0.4% hydrochloric acid (HCl) and stored dark, in a refrigerator at a temperature between 0-4°C until distillation.

12.3 Acid-preserved samples are stable for at least six months, if kept dark and cool (EPA 1630).

13) Apparatus and Equipment:

13.1 LIMS – TALS (current production version); Computer – Windows 7 or higher

13.2 Tekran 2750 Distillation Apparatus with appropriate Teflon distillation vials. Receiving vials must be marked to approximately 40 mL. This mark is not quantitative.

13.3 Sampling Bottles: It is imperative for accurate sub-ng/L MHg measurements that PETG bottles or appropriately cleaned Teflon bottles or glass bottles, with Teflon-lined, tight-fitting lids are used for all steps contacting the sample. These bottles are washed according to SOP EFGS-007, "Cleaning of Sampling Equipment and Bottles for Mercury Analysis."

13.4 Pipettors: All-plastic, pneumatic, fixed volume and variable pipettes in the range of 20 µL to 10 mL. Pipettes are to be calibrated weekly according to SOP *EFGS-Q-QD-SOP41510*.

13.5 pH paper: paper with the range appropriate to evaluating the pre and post distillation pH checks. Ideally 0 to 7.

13.6 Clean hood.

13.7 Analytical Balance: A laboratory analytical balance that measures accurately to 0.01mg, with documented calibration.

14) Reagents and Standards:

14.1 Reagent Water: 18 MW ultra-pure deionized water starting from a pre-purified (distilled, R.O., etc.) source. As a final mercury and organic removal step, the activated carbon cartridge on the 18-MW system is placed between the final ion exchange bed and the 0.2 µm filter.

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14.1.1 Pipette tip rinse bottle labeled:

Speciation Rinse, MQ only

To be used for all speciation analysis: As, DMHg, CrVI, HgO, MHg, Se and any other type of speciation analysis. Anything that requires us to evaluate an oxidation state of any metal.

14.2 Hydrochloric Acid: Trace metal purified reagent-grade HCl is pre-analyzed and lot sequestered. Several brands (Baker, Fisher, Omnitrace) have been found to have lots with acceptably low levels of trace metals. This reagent should be from a lot number that has been previously tested to be low for the analytes of interest. This reagent shall be entered into LIMS and the expiration date is set to the same as the manufacturer's expiration date.

14.2.1 0.4% Hydrochloric Acid: In a designated Teflon bottle, 995 ± 25mL reagent water is weighed out and 4 mL of HCl is measured out with a pipette or re-pipettor. Solution must be made fresh prior to each distillation. This may be made at alternative final volumes so long as reagent ratios are kept constant.

14.3 1% APDC Solution: To 100 mL of reagent water, add 1.0 g of reagent-grade ammonium pyrrolidine dithiocarbamate (APDC), and shake to dissolve. Add 10 mL of methylene chloride, and shake for two minutes. Let stand for 15 minutes and then decant the top layer into a clean bottle. The solution is then stored in refrigerator. The solution is entered into LIMS with a holding time of 1 week. This may be made at alternative final volumes so long as reagent ratios are kept constant.

14.4 Argon - Standard laboratory grade

15) Procedure:

15.1 Samples are collected and handled according to SOP *EFGS-S-CS-SOP2794*, "Ultra Clean Aqueous Sample Collection."

15.2 Obtain pairs of clean sample and receiving distillation vials. Empty the contents of the vials into a large beaker with sodium bicarbonate. Rinse each vial three times with reagent water, making sure to rinse the lids and tubes thoroughly.

15.3 Attach argon supply line to 2750 unit (pressure to unit should be approximately 60 psi, regulator on unit should be 42 psi). Turn on digestion unit and set temperature to 122 C.

15.4 Retrieve the samples to be distilled from the walk-in refrigerator. Organize the samples in the same order as they are listed on the LIMS bench sheet, and make sure that all samples are accounted for.

15.5 Tape labels onto the receiving vials so the bottom of the label is just touching the top of the 40.0-mL engraved mark. Pipette 5 mL of reagent water into each of the receiving vials, so that the bottom of the tubing is covered.

15.6 Check the pH of each sample by removing a small aliquot with a clean pipet and dispensing the aliquot on pH paper. The samples should be acidic (< pH 2). If the pH is greater than or equal to 2, add concentrated hydrochloric acid (HCl) dropwise until the pH is less than 2. Document the pH and note any adjustments in the sample distillation logbook.

15.7 Each sample vial is placed on the balance and tared before adding up to 50.0 ± 0.2 g of sample (enter 50 mL as the initial volume in this case in the LIMS). A smaller aliquot volume may be used if samples are suspected to be high in MHg, or if there is a limited amount of sample available. These smaller aliquots are diluted to 50 mL with the 0.4% HCl. If a smaller aliquot is used, the aliquot volume is entered as the initial volume in the LIMS.

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Note: For samples that are suspected to have densities that are not 1.00 ± 0.02 g/mL, the density must be determined and the aliquot size must be adjusted to accommodate this difference between mass and volume.

15.8 Prepare three blanks, one blank spike, and one blank spike duplicate at 50 mL using 0.4% HCl as the diluent.

15.9 Using a pipette add 200 µL of 1% APDC to each vial (sample and QC) before capping the vial. The sample vial is then placed next to its corresponding receiving vial in a holding rack. Record the LIMS ID of the APDC solution in the logbook.

15.10 After all samples are prepared, spike 50 µL of 1.0 ng/mL standard into the blank spike and matrix spike samples for a true value of 1.0 ng/L. The LIMS ID of the standard used for spiking must be added to LIMS bench sheet. Note: Spike amount listed is a suggestion and may be adjusted if necessary.

15.10.1 Due to the lack of a CRM for methyl mercury in water, at least one blank spike/blank spike duplicate must be analyzed per analytical batch.

15.11 Turn on chilled water batch as well and allow to be on for at least 30 minutes before placing samples in it. Do not allow the batch to be on for longer than this without placing samples in it, as the water will freeze.

15.12 Place the receiving vessel into the ice-water bath and its sample vial counterpart into the corresponding heating block hole. The tubing from the receiving vial is placed into the hole in the cap of the sample vial, and the tubing from the sample vial is plugged into the airflow bank. Teflon tape is used to ensure a snug fit on the tubing. After all vials are in a block, the aluminum cover piece is placed over the sample vials.

15.13 A distillation rate of 10-15 mL per hour should be maintained, until a total volume of 40 ± 1 mL is achieved in a receiving vial. The distillation is complete when the water line in the receiving vial reaches the bottom of the label on the receiving vessel. The receiving vial is then disconnected from the sample vial and brought to a final volume of 50 mL using distilled water in a clean centrifuge tube. The distillation for a water sample of 40 mL should take approximately 2.5-4 hours.

15.14 The pH is measured for all samples and is recorded in the LIMS.

15.15 The optimum pH for the distillate is 3.5-7. For pH <3.0, the sample will be analyzed, but should be re-distilled if sufficient sample volume remains. Tests have shown that reasonable recoveries are still maintained with lower pH distillates.

15.16 The distillate may then be analyzed using aqueous phase ethylation, GC separation, and CVAFS detection. For water samples, the entire sample will usually be analyzed. Calculation of MHg content is based upon the actual volume of sample distilled corrected by the empirically derived distillation efficiency factor. For samples determined to be possibly high in MHg, a fraction of the total distillate may be analyzed.

16) Calculations:

16.1 This preparation procedure does not involve calculations.

17) Statistical Information/Method Performance:

17.1 Method Detections Limits (MDL) are determined during method development and then annually thereafter according to 40 CFR Part 136, Section B and *CA-Q-S-006*.

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17.2 The Practical Quantitation Limit (PQL) is the reporting limit for this method and is included as the lowest calibration point (2003 NELAC regulation 5.5.5.2.2.1.h.3).

17.3 Current control limits and reporting limits can be found in the LIMS.

18) Quality Assurance/Quality Control:

18.1 Maximum Sample Batch Size: 20 samples.

18.2 Preparation Blanks: Minimum of three per batch. Each preparation blank must be less than the PQL for the method.

18.2.1 The preparation blanks are prepared using the 0.4% HCl diluent; these are put through the same preparation process as the samples.

18.3 Certified Reference Material (CRM, representing the sample matrix when commercially available); or a Laboratory Control Spike (LCS) and Laboratory Control Spike Duplicate (LCSD) is used when a suitable CRM is not available: One per batch in duplicate. The control limits are 65-135% recovery.

18.4 Matrix Duplicate (MD): Not required. A Matrix Duplicate (MD) may be analyzed for every batch of 20 samples upon client request. The control limit for the RPD is <=35%.

18.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Samples: One set per 10 samples. The control limits are 65-135% recoveries and an RPD of <= 35%.

18.6 Follow the flow charts in SOP *EFGS-P-DR-SOP2801* "Data Review and Validation" to determine if any QC falling outside the established control limits can be qualified.

18.7 All of the quality control limits for the analysis method are included on the "Data Review Checklist" in the LIMS.

19) Corrective Action:

19.1 Limiting the source of contamination/error in the preparatory stage can decrease QC problems during analysis. Limiting such contamination/error sources may include: cleaning all digestion tools in a 10% HCl solution, ensuring all samples are thoroughly homogenized, changing gloves whenever appropriate, flushing repipettors at least three times before dispensing into vials and, in general, following ultra-clean procedures.

19.2 A failing QC point does not necessary fail the entire dataset. If upon analysis a QC sample is out of control, some investigation must be performed to assess if the difficulties are related to matrix effects. The cause and method of determining the set's failure must be documented on the checklist and in the MMO notes, and the Group Supervisor shall be informed. See SOP *EFGS-P-DR-SOP2801* "Data Review and Validation" for flow charts regarding analytical issues.

19.3 If a matrix spike sample does not show recovery within the control limits, it is possible that the sample was not spiked properly. The analyst preparing the samples should review the spiking level for accuracy. Spikes are always witnessed by a peer who then initials/dates the logbook.

19.4 If contamination is suspected to be a problem, the vials may need to be deep cleaned using BrCl. Additionally, reagents should be checked for contamination or remade in clean bottles.

19.5 If samples render abnormal results, several other variables should be investigated to discover the source of error. The Senior Analyst, and/or the Group Supervisor should be consulted to discuss possible areas for trouble-shooting.

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19.5.1 Check for a loose connection or air leak in the tubing connecting the vials, and check to ensure that all vial caps were screwed on tightly during the distillation process.

19.5.2 The temperature of the heating blocks should be checked and, if necessary, adjusted within the range of 120°C and 125°C.

19.5.3 Airflow should also be checked to ensure that it is functioning.

19.6 If the distillation process is determined to be the cause of the analytical problems, then all samples with sufficient volume must be re-distilled. Samples without sufficient volume will be flagged during the review process and then narrated in the case narrative by the Project Manager.

EFGS-P-DR-SOP2801 Data Review and Validation and Monthly Logbook Reviews
EFGS-Q-QM-QM5805 Quality Assurance Manual
EFGS-S-CS-SOP2794 Ultra-Clean Aqueous Sample Collection
EFGS-S-HS-QP12066.0004 Chemical Hygiene Plan
EFGS-S-HS-SOP2991 Waste Disposal Procedures for Client Sample Waste
EFGS-T-AFS-SOP2808 Determination of Methyl Mercury in Various Matrices by CV–GC–AFS
EFQA-Q-QD-SOP10098 Procedures for Determining IDLs, MDLs, LODs, PQLs, LOQs, OPRs, IQs, OQs and PQs
EFQA-Q-QD-SOP2711 Pipette and Dispenser: Operation, Calibration & Maintenance

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Quality Assurance Manual

Eurofins Seattle
5755 8th Street East
Tacoma, WA 98424
Phone No. (253) 922-2310
Fax No. (253) 922-5047
https://www.eurofinsus.com

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1) INTRODUCTION, SCOPE AND APPLICABILITY

1.1) Introduction and Compliance References

Eurofins Seattle's Quality Assurance (QA) Manual is a document prepared to define the overall policies, organization objectives and functional responsibilities for achieving the laboratory's QA Program. Governing SOPs are in place within the organization to ensure the proper execution of this QA Manual (refer to Appendix 1). This manual and referenced documents are required reading for all personnel.

The laboratory is a team of people who work together to serve the health and environmental needs of society through science and technology. We comprehensive expertise in environmental laboratory applications, low-level mercury, trace metals and metals speciation in environmental and industrial matrices and client relations and maintain a national perspective in terms of quality.

As such, this QA Manual has been prepared to assure compliance with The NELAC Institute (TNI) Standard, dated 2009 and 2016; ISO/IEC Guide 17025: 2005 and 2017 and the Department of Defense (DoD)/Department of Energy (DOE) Quality Systems Manual (QSM). Policies and procedures listed in Appendix 1 are compliant with the National Divisional Support Center (NDSC) Quality Management Plan (QMP) for Eurofins Environmental Testing America and the various accreditation and certification programs which are held by the laboratory to support environmental work (Appendix 2). The QMP provides a summary of Eurofins Environmental Testing America quality

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and data integrity system. It contains requirements and general guidelines under which all Eurofins Environmental Testing America facilities shall conduct their operations.

Refer to Appendix 3 for a list of additional references for which this QA Manual is compliant; and Appendix 4 for the compliance crosswalk of this manual to the TNI & ISO/IEC Guide 17025 requirements.

1.2) Terms and Definitions

A QA Program is a system designed to ensure that data produced by the laboratory conforms to the standards set by state and/or federal regulations. The program functions at the local management level through company goals, from guidance at the executive management level, and at the analytical level through Standard Operating Procedures (SOPs) and quality control. Our program is designed to minimize systematic error, encourage constructive, documented problem solving, and provide a framework for continuous improvement within the organization to better serve our clients.

Refer to Appendix 5 for a list of Terms and Acronyms.

1.3) Scope / Fields of Testing

The laboratory analyzes a broad range of environmental and industrial samples. Sample matrices vary among effluent water, groundwater, hazardous waste, sludge and soils. The Program contains specific procedures and methods to test samples of differing matrices for chemical, physical and biological parameters. The Program also contains guidelines on maintaining documentation of analytical processes, reviewing results, servicing clients and tracking samples through the laboratory. The technical and service requirements of all analytical requests are thoroughly evaluated before commitments are made to accept the work. Measurements are made using published reference methods or methods developed and validated by the laboratory.

The methods covered by this manual include the most frequently requested methodologies needed to provide analytical services in the United States and its territories. The specific list of test methods used by the laboratory can be found in the Laboratory Information Management System (LIMS). Our areas of expertise include:

Standard Services	Specialty Services
• Volatiles • Semivolatiles • Metals • Pesticides/PCBs • Petroleum Hydrocarbons • Waste Characterization • Non-Potable Water Testing • Soil and Surface Water Testing • Sediment and Tissue Testing	• Low-level Mercury • Trace Metals • Metals Speciation • Air Analysis

Note: All current certificates and scopes of accreditation are available on the laboratory's website at https://www.eurofinsus.com/environment-testing/resources/certifications/.

The approach of this manual is to define the minimum level of quality assurance and quality control necessary to meet these requirements. All methods performed by the laboratory shall meet these criteria as appropriate. In some instances, quality assurance project plans (QAPPs), project specific data quality objectives (DQOs) or local regulations may require criteria other than those contained in this manual. In these cases, the laboratory will abide by the requested criteria following review and acceptance of the requirements by the Laboratory President, Laboratory Vice-President, Director of Operations, Business Unit Manager and the Quality Assurance (QA) Manager. In some cases, QAPPs and DQOs may specify less stringent requirements. The Laboratory President, Laboratory Vice-President, Director of Operations, Business Unit Manager and the QA Manager must determine if it is in the lab's best interest to follow the less stringent requirements.

1.4) Management of the Manual

1.4.1) Review Process

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The template on which this manual is based is reviewed annually by Eurofins National Divisional Support Center (NDSC), which houses the Quality Assurance leadership team for Eurofins Environment Testing America. NDSC QA will assure that the template remains in compliance with Section 3.1. This manual itself is reviewed annually by senior laboratory management to assure that it reflects current practices and meets the requirements of the laboratory's clients and regulators as well as the QMP. Occasionally, the manual may need changes in order to meet new or changing regulations and operations. The QA Manager will review the changes in the normal course of business and incorporate changes into revised sections of the document. All updates will be reviewed by the senior laboratory management staff. The laboratory updates and approves such changes according to our Document Control & Updating procedures (refer to SOP No. *EFGS-Q-QD-SOP2804* and *EFGS-Q-QD-SOP2802*).

2) MANAGEMENT REQUIREMENTS

2.1) Overview

The laboratory is a local operating unit of Eurofins Environment Testing America. The laboratory's operational and support staff have the day-to-day independent operational authority under the direction of the Laboratory President, Laboratory Vice-President, Director of Operations, Laboratory Director and/or Business Unit Manager and is supported by the NDSC QA team. The laboratory management staff includes directors, managers and group leaders. The organizational chart of the management staff are presented in Figure 2-1. Individual departmental staff lists are maintained in the laboratory's internal intranet.

2.2) Roles and Responsibilities

In order for the QA Program to function properly, all members of the staff must clearly understand and meet their individual responsibilities as they relate to the quality program. The responsibility for quality resides with every employee of the laboratory. All employees have access to the QA Manual, are trained to this manual, and are responsible for upholding the standards therein. Each person carries out his/her daily tasks impartially and in a manner consistent with the goals and in accordance with the procedures in this manual and the laboratory's SOPs. The following descriptions briefly define each role in its relationship to the Quality Assurance Program.

2.2.1) Vice President of Quality and Environmental Health and Safety (VP-QA/EHS)

The Vice President (VP) of QA/EHS reports directly to Eurofins Environment Testing America Chief Operating Officer (COO). With the aid of the NDSC Quality Team Members, Business Unit Managers, Laboratory Directors, the VP-QA/EHS has the responsibility for the establishment, general overview and maintenance of the Quality Assurance and EH&S Programs within Eurofins Environment Testing America. Additional responsibilities include:

- Review of QA/QC and EHS aspects of NDSC Official Document, national projects and expansions or changes in services.
- Work with various organizations outside of the laboratory to further the development of quality standards and represent the laboratory at various trade meetings.
- Prepare monthly reports for quality and EH&S metrics across the environmental testing laboratories and a summary of any quality and EH&S related initiatives and issues.
- With the assistance of the Executive Management, and the EHS Managers, maintenance and implementation of the Eurofins Environment Testing America Environmental, Health and Safety Program.

2.2.2) Quality Directors

There are three (3) Quality Directors within NDSC that report directly to the VP-QA/EHS. These Quality Directors have oversight of the general overview and maintenance of the QA Program within the Eurofins Environment Testing America laboratories. Supported tasks include:

- Monitors laboratory internal audit findings;
- Identifies common laboratory weaknesses and monitors corrective action closures.
- Develops NDSC quality guidance documents and management tools for ensuring and improving compliance;
- Monitors and communicates DoD/DoE requirements;

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- Monitors and communicates regulatory and certification requirements;
- Training and OnBoarding
- Laboratory assessments, mentoring, and interventions
- Track/drive root cause investigations and corrective action plans
- Builds knowledge base for preventive actions

2.2.3) Quality Information Manager

The Quality Information works directly with the NDSC Quality Directors and EHS Managers; and reports directly to the VP-QA/EHS. The Quality Information Manager is responsible for the management of:

- NDSC Official Documents
- TALS/LIMS Certification Module Data
- Company's Intranet website
- Company's Regulatory Limits Database
- Subcontract laboratory and approved vendor information
- Internal and External client support for various company groups (e.g., Client Services, EH&S, Legal, IT, Sales) for both quality and operational functions
- Communicate regulatory information and lists

2.2.4) Environmental Health and Safety (EH&S) Managers

There are 3 EH&S Managers within NDSC that report directly to the VP-QA/EHS. These EH&S Managers have oversight of the general overview and maintenance of the EH&S Program within the Eurofins Environment Testing America laboratories. Supported tasks include:

- Consolidation and tracking all safety and health-related information and reports for the company, and managing compliance activities for Eurofins Environment Testing America locations.
- Coordination/preparation of the Environmental, Health and Safety Manual Template that is used by each laboratory to prepare its own laboratory-specific Safety Manual/ CHP.
- Preparation of information and training materials for laboratory EHS Coordinators.
- Assistance in the coordination of employee exposure and medical monitoring programs to insure compliance with applicable safety and health regulations.
- Serving as Department of Transportation (D.O.T.) focal point and providing technical assistance to location management.
- Serving as Hazardous Waste Management main contact and providing technical assistance to location management.

2.2.5) Ethics and Compliance Officers (ECOs)

The NDSC VP-QA/EHS and Corporate Counsel are designated Ethics and Compliance Officer (ECO). Each ECO acts as a back-up to the other ECO and both are involved when data investigations occur. Each ECO has a direct line of communication to the entire executive management personnel and lab management staff.

The ECOs monitor and audit procedures to determine compliance with policies and to make recommendations for policy enhancements to the President, COO, Laboratory Director or other appropriate individuals within the laboratory. The ECO will assist the laboratory QA Manager in the coordination of internal auditing of ethical policy related activities and processes within the laboratory, in conjunction with the laboratory's regular internal auditing function.

The ECOs will also participate in investigations of alleged violations of policies and work with the appropriate internal departments to investigate misconduct, remedy the situation, and prevent recurrence of any such activity.

2.2.6) Business Unit Manager (BUMA)

The BUMA is responsible for the overall quality, safety, financial, technical, human resource and service performance of the whole laboratory and reports to their business unit President. The BUMA is also responsible for any service centers connected with their laboratory that perform analytical tests, such as short holding time analyses for pH. The BUMA provides the resources necessary to implement and maintain an effective and comprehensive Quality Assurance and Data Integrity Program.

Specific responsibilities include, but are not limited to:

- Provides one or more technical managers for the appropriate fields of testing. If the Technical Manager is absent for a period of time exceeding 15 consecutive calendar days, the Laboratory Director must designate another full time staff member meeting the qualifications of the Technical Manager to temporarily perform this function. If the absence exceeds 35 consecutive calendar days, the primary accrediting authority must be notified in writing.
- Ensures that all analysts and supervisors have the appropriate education and training to properly carry out the duties assigned to them and ensures that this training has been documented. Works with Eurofins Environment Testing Human Resources for hiring of new personnel.
- Ensures that personnel are free from any commercial, financial and other undue pressures which might adversely affect the quality of their work.
- Ensures company human resource policies are adhered to and maintained.
- Ensures that sufficient numbers of qualified personnel are employed to supervise and perform the work of the laboratory. Assesses laboratory capacity and workload.
- Ensures that appropriate corrective actions are taken to address analyses identified as requiring such actions by internal and external performance or procedural audits. Procedures that do not meet the standards set forth in the QA Manual or laboratory SOPs may be temporarily suspended by the Laboratory Director.
- Reviews and approves all SOPs prior to their implementation and ensures all approved SOPs are implemented and adhered to.
- Pursues and maintains appropriate laboratory certification and contract approvals. Supports ISO 17025 requirements.
- Ensures client specific reporting and quality control requirements are met.
- Contributes to the continuous improvement of the laboratory operations.
- Maintains an awareness of technical developments and regulatory requirements.
- Captains the management team, consisting of the QA Manager, the Technical Manager(s), and the Operations Manager as direct reports.

2.2.7) Quality Assurance (QA) Manager or Designee

The QA Manager has responsibility and authority to ensure the continuous implementation of the quality system at the laboratory where they work. The QA Manager is also responsible for any service centers connected with their laboratory that perform analytical tests, such as short holding time analyses for pH.

The QA Manager reports directly to the Laboratory Director/BUMA and their NDSC Quality Director. This position is able to evaluate data objectively and perform assessments without outside (e.g., managerial) influence. The NDSC QA Team may be used as a resource in dealing with regulatory requirements, certifications and other quality assurance related items. The QA Manager directs the activities of the QA officer to accomplish specific responsibilities, which include, but are not limited to:

- Serves as the focal point for QA/QC in the laboratory.
- Have functions independent from laboratory operations for which he/she has quality assurance oversight.
- Have documented training and/or experience in QA/QC procedures and the laboratory's Quality System.
- Have a general knowledge of the analytical test methods for which data audit/review is performed (and/or having the means of getting this information when needed).
- Arrange for or conducting internal audits on quality systems and the technical operation
- Notifying laboratory management of deficiencies in the quality system and ensuring corrective action is taken. Procedures that do not meet the standards set forth in the QA Manual or laboratory SOPs shall be investigated following procedures outlined in Section 14 and if deemed necessary may be temporarily suspended during the investigation.
- Maintaining and updating the QA Manual.
- Monitoring and evaluating laboratory certifications; scheduling proficiency testing samples.
- Monitoring and communicating regulatory changes that may affect the laboratory to management.
- Training and advising the laboratory staff on quality assurance/quality control procedures that are pertinent to their daily activities.
- The laboratory QA Manager will maintain records of all ethics-related training, including the type and proof of attendance.

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- Maintain, improve, and evaluate the corrective action database and the corrective and preventive action systems.
- Objectively monitor standards of performance in quality control and quality assurance without outside (e.g., managerial) influence.
- Coordinating of document control of SOPs, MDLs, control limits, and miscellaneous forms and information.
- Performing technical data audits and method audits to ensure consistency and compliance with regulatory requirements.
- Review of external audit reports and data validation requests.
- Follow-up with audits to ensure client QAPP requirements are met.
- Establishment of reporting schedule and preparation of various quality reports for the Laboratory Director, clients and/or NDSC QA Team.
- Development of suggestions and recommendations to improve quality systems.
- Research of current state and federal requirements and guidelines.
- Participate in the vendor and supplier approval process, including subcontractors.
- Captains the QA team to enable communication and to distribute duties and responsibilities.
- Communication to the relevant regulatory authorities when there are management or facility changes that impact the laboratory.
- Ensuring communication & monitoring standards of performance to ensure that systems are in place to produce the level of quality as defined in this document.
- Evaluation of the thoroughness and effectiveness of training.
- Compliance with ISO 17025
- Compliance with the DoD/DOE QSM.

2.2.8) Technical Manager or Designee

The Technical Manager(s) report(s) directly to the BUMA. He/she is accountable for all analyses and analysts under their experienced supervision and for compliance with the ISO 17025:2017 Standard. The scope of responsibility ranges from the new-hire process and existing technology through the ongoing training and development programs for existing analysts and new instrumentation. Specific responsibilities include, but are not limited to:

- Exercises day-to-day supervision of laboratory operations for the appropriate field of accreditation and reporting of results. Coordinating, writing, and reviewing preparation of all test methods, i. e., SOPs, with regard to quality, integrity, regulatory and optimum and efficient production techniques, and subsequent analyst training and interpretation of the SOPs for implementation and unusual project samples. He/she insures that the SOPs are properly managed and adhered to at the bench. He/she develops standard costing of SOPs to include supplies, labor, overhead, and capacity (design vs. demonstrated versus first-run yield) utilization.
- Reviewing and approving, with input from the QA Manager, proposals from marketing, in accordance with an established procedure for the review of requests and contracts. This procedure addresses the adequate definition of methods to be used for analysis and any limitations, the laboratory's capability and resources, the client's expectations. Differences are resolved before the contract is signed and work begins. A system documenting any significant changes is maintained, as well as pertinent discussions with the client regarding their requirements or the results of the analyses during the performance of the contract. All work subcontracted by the laboratory must be approved by the client. Any deviations from the contract must be disclosed to the client. Once the work has begun, any amendments to the contract must be discussed with the client and so documented.
- Monitoring the validity of the analyses performed and data generated in the laboratory. This activity begins with reviewing and supporting all new business contracts, insuring data quality, analyzing internal and external non-conformances to identify root cause issues and implementing the resulting corrective and preventive actions, facilitating the data review process (training, development, and accountability at the bench), and providing technical and troubleshooting expertise on routine and unusual or complex problems.
- Providing training and development programs to applicable laboratory staff as new hires and, subsequently, on a scheduled basis. Training includes instruction on calculations, instrumentation management to include troubleshooting and preventive maintenance.
- Enhancing efficiency and improving quality through technical advances and improved LIMS utilization. Capital forecasting and instrument life cycle planning for second generation methods and instruments as well as asset inventory management.
- Coordinating sample management from "cradle to grave," insuring that no time is lost in locating samples.
- Scheduling all QA/QC-related requirements for compliance, e.g., MDLs, etc.

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- Captains department personnel to communicate quality, technical, personnel, and instrumental issues for a consistent team approach.
- Coordinates audit responses with the QA Manager.
- Compliance with ISO 17025.
- Compliance with the DoD/DOE QSM.

2.2.9) Operations Manager

The Operations Manager manages and directs the analytical production sections of the laboratory. He/She reports directly to the Laboratory Director. He/She assists the Technical Manager in determining the most efficient instrument utilization. More specifically, he/she:

- Evaluates the level of internal/external non-conformances for all departments.
- Continuously evaluates production capacity and improves capacity utilization.
- Continuously evaluates turnaround time and addresses any problems that may hinder meeting the required and committed turnaround time from the various departments.
- Develops and improves the training of all analysts in cooperation with the Technical Manager and QA Manager and in compliance with regulatory requirements.
- Works with the Preventive Maintenance Coordinator to ensure that scheduled instrument maintenance is completed.
- Is responsible for efficient utilization of supplies.
- Constantly monitors and modifies the processing of samples through the departments.
- Fully supports the quality system and, if called upon in the absence of the QA Manager, serves as his substitute in the interim.

2.2.10) Client Services Manager

The Client Services Manager reports to the Business Unit Manager and serves as the interface between the laboratory's technical departments and the laboratory's clients. The staff consists of the Project Management team. With the overall goal of total client satisfaction, the functions of this position are outlined below:

- Technical training and growth of the Project Management team.
- Technical liaison for the Project Management team.
- Human resource management of the Project Management team.
- Has signature authority for laboratory reports.
- Assesses and assures customer satisfaction.
- Provides feedback to management on changing customer needs.
- Works with the Department Managers and/or Analysts/Technicians to ensure the requirements of projects are met in a timely manner.
- Organizes bid activities for prospective new projects and clients.

2.2.11) Project Manager (PM)

Members of the laboratory Client Services/Project Management Group are responsible for organizing and managing client projects. Clients are assigned a project manager who serves as their primary contact at the laboratory. It is the PM's responsibility to act as the client advocate by communicating client requirements to laboratory personnel and ensuring that clients provide complete information needed by the laboratory to meet those requirements – including all verbal communications.

- Scheduling sample submissions, sample container orders and sample pick-up via the laboratory courier service.
- Confirming certification status
- Coordinating and communicating turnaround time (TAT) requirements for high priority samples/projects.
- Answering common technical questions, facilitating problem resolution and coordinating technical details with the laboratory staff.
- Ensuring that client specifications, when known, are met by communicating project and quality assurance requirements to the laboratory.
- Notifying the supervisors of incoming projects and sample delivery schedules.
- Accountable to clients for communicating sample status reports or results prior to receipt of the final report.
- Monitor the status of all data package projects in-house to ensure timely and accurate delivery of reports.

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- Inform clients of data package-related problems and resolve service issues.

2.2.12) Department Supervisors/Manager

Supervisors/Managers report to the Operations Manager. Each one is responsible to:

- Ensure that analysts in their department adhere to applicable SOPs and the QA Manual. They perform frequent SOP and QA Manual review to determine if analysts are in compliance and if new, modified, and optimized measures are feasible and should be added to these documents.
- With regard to analysts, participates in the selection, training (as documented in Section 3.3), development of performance objectives and standards of performance, appraisal (measurement of objectives), scheduling, counseling, discipline, and motivation of analysts and documents these activities in accordance with systems developed by the QA and Personnel Departments. They evaluate staffing sufficiency and overtime needs. Training consists of familiarization with SOP, QC, Safety, and computer systems.
- Encourage the development of analysts to become cross-trained in various methods and/or operate multiple instruments efficiently while performing maintenance and documentation, self-supervise, and function as a department team.
- Provide guidance to analysts in resolving problems encountered daily during sample prep/analysis in conjunction with the Technical Manager, Operations Manager, and/or QA Manager. Each is responsible for 100% of the data review and documentation, non-conformance and CPAR issues, the timely and accurate completion of performance evaluation samples and MDLs, for his department.
- Ensure all logbooks are maintained, current, and properly labeled or archived.
- Report all non-conformance conditions to the QA Manager, Technical Manager, Operations Manager, and/or BU / Laboratory Director.
- Ensure that preventive maintenance is performed on instrumentation as detailed in the QA Manual or SOPs. He is responsible for developing and implementing a system for preventive maintenance, troubleshooting, and repairing or arranging for repair of instruments.
- Maintain adequate and valid inventory of reagents, standards, spare parts, and other relevant resources required to perform daily analysis.
- Achieve optimum turnaround time on analyses and compliance with holding times.
- Conduct efficiency and cost control evaluations on an ongoing basis to determine optimization of labor, supplies, overtime, first-run yield, capacity (designed vs. demonstrated), second- and third-generation production techniques/instruments, and long-term needs for budgetary planning.
- Develop, implement, and enhance calibration programs.
- Provide written responses to external and internal audit issues.

2.2.13) Laboratory Analysts

Laboratory analysts are responsible for conducting analysis and performing all tasks assigned to them by the group leader or supervisor. The responsibilities of the analysts are listed below:

- Perform analyses by adhering to analytical and quality control protocols prescribed by current SOPs, this QA Manual, and project-specific plans honestly, accurately, timely, safely, and in the most cost-effective manner.
- Document standard and sample preparation, instrument calibration and maintenance, data calculations, sample matrix effects, and any observed non-conformance on worklists, benchsheets, lab notebooks and/or the Non-Conformance Database.
- Report all non-conformance situations, instrument problems, matrix problems and QC failures, which might affect the reliability of the data, to their supervisor, the Technical Manager, and/or the QA Manager or member of QA staff.
- Perform 100% review of the data generated prior to entering and submitting for secondary level review.
- Suggest method improvements to their supervisor, the Technical Manager, and the QA Manager. These improvements, if approved, will be incorporated. Ideas for the optimum performance of their assigned area, for example, through the proper cleaning and maintenance of the assigned instruments and equipment, are encouraged.
- Work cohesively as a team in their department to achieve the goals of accurate results, optimum turnaround time, cost effectiveness, cleanliness, complete documentation, and personal knowledge of environmental analysis.

2.2.14) Safety Officer

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The Safety Officer reports to the BUMA and ensures that systems are maintained for the safe operation of the laboratory. The Safety Officer is responsible to:

- Conduct ongoing, necessary safety training and conduct new employee safety orientation.
- Assist in developing and maintaining the Chemical Hygiene/Safety Manual.
- Administer dispersal of all Material Safety Data Sheet (MSDS) information.
- Perform regular chemical hygiene and housekeeping instruction.
- Give instruction on proper labeling and practice.
- Serve as chairman of the laboratory safety committee.
- Provide and train personnel on protective equipment.
- Oversee the inspection and maintenance of general safety equipment – fire extinguishers, safety showers, eyewash fountains, etc. and ensure prompt repairs as needed.
- Supervise and schedule fire drills and emergency evacuation drills.
- Determine what initial and subsequent exposure monitoring, if necessary to determine potential employee exposure to chemicals used in the laboratory.
- When determined necessary, conduct exposure monitoring assessments.
- Determine when a complaint of possible over-exposure is "reasonable" and should be referred for medical consultation.
- Assist in the internal and external coordination of the medical consultation/monitoring program conducted by Eurofins medical consultants.

2.2.15) Sample Receiving Staff

The Sample Receiving Technicians report to the Sample Receiving Supervisor; the Supervisor reports to the Operations Manager. The responsibilities are outlined below:

- Ensures implementation of proper sample receipt procedures, including maintenance of chain-of-custody.
- Reports non-conformances associated with condition-upon-receipt of samples.
- Logs incoming samples into the LIMS.
- Ensures that all samples are stored in the proper environment.
- Ensure the verification of data entry from login.
- Responsible for meeting quality requirements including documenting preservation.
- Responsible for ensuring the timely and correct shipment of sample containers, including proper preservatives and instructions, to clients

2.3) Business Continuity and Contingency Plans

Various policies and practices are in place to address continuity of business and contingency plans to ensure continued operations or minimal disruption in operations should unplanned events (natural disasters, unexpected management changes, etc.) occur. Deputies are identified for all key management personnel. Deputies would temporarily fill a role if the primary is absent for more than 15 consecutive calendar days. The deputies must meet the same qualifications as the primary person should they be required to take on the responsibilities. The QA Manager communicates to the relevant regulatory authorities when there are management or facility changes that impact the laboratory. Changes in the technical director must be communicated within a period of time and in the manner dictated by each regulatory authority.

The following table defines who assumes the responsibilities of key personnel in their absence:

Key Personnel	Deputy
BUMA	President
QA Manager	BUMA
Scientific Support Specialist (Technical Manager)	BUMA
Lab Manager	Scientific Support Specialist
Operations Manager	BUMA
Department Supervisor/Manager	Operations Manager

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Key Personnel	Deputy
EHS Coordinator	BUMA
Client Services Manager	BUMA

2.3) Figure 2-1. Laboratory Organization Charts
see ***EFGS-M-OC-FRM46125***

3) PERSONNEL
3.1) Overview
The laboratory's management believes that its highly qualified and professional staff is the single most important aspect in assuring a high level of data quality and service. The staff consists of professionals and support personnel.

All personnel must demonstrate competence in the areas where they have responsibility. Any staff that is undergoing training shall have appropriate supervision until they have demonstrated their ability to perform their job function on their own. Staff shall be qualified for their tasks based on appropriate education, training, experience and/or demonstrated skills as required.

The laboratory employs sufficient personnel with the necessary education, training, technical knowledge and experience for their assigned responsibilities.

All personnel are responsible for complying with all QA/QC requirements that pertain to the laboratory and their area of responsibility. Each staff member must have a combination of experience and education to adequately demonstrate a specific knowledge of their particular area of responsibility. Technical staff must also have a general knowledge of lab operations, test methods, QA/QC procedures and records management.

Laboratory management is responsible for formulating goals for lab staff with respect to education, training and skills and ensuring that the laboratory has a policy and procedures for identifying training needs and providing training of personnel. The training shall be relevant to the present and anticipated responsibilities of the lab staff.

The laboratory only uses personnel that are employed by or under contract to, the laboratory. Contracted personnel, when used, must meet competency standards of the laboratory and work in accordance to the laboratory's quality system.

3.2) Education and Experience Requirements for Technical Personnel
The laboratory makes every effort to hire analytical staffs that possess a college degree (AA, BA, BS) in an applied science with some chemistry in the curriculum. Exceptions can be made based upon the individual's experience and ability to learn. Selection of qualified candidates for laboratory employment begins with documentation of minimum education, training, and experience prerequisites needed to perform the prescribed task. Minimum education and training requirements for laboratory employees are outlined in job descriptions maintained by Eurofins Environment Testing America Human Resources.

Experience and specialized training are occasionally accepted in lieu of a college degree (basic lab skills such as using a balance, colony counting, aseptic or quantitation techniques, etc., are also considered).

As a general rule for analytical staff:

Specialty	Education	Experience
Digestions, some electrode methods (pH, DO, Redox, etc.), or Titrimetric and Gravimetric Analyses	H.S. Diploma	On the job training (OJT)

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Specialty	Education	Experience
GFAA, CVAA, FLAA, Single component or short list Chromatography (e.g., Fuels, BTEX-GC, IC)	A college degree in an applied science or 2 years of college and at least 1 year of college chemistry	Or 2 years prior analytical experience is required
ICP, ICPMS, Long List or complex chromatography (e.g., Pesticides, PCB, Herbicides, HPLC, etc.), GCMS, GCMS-MS	A college degree in an applied science or 2 years of college chemistry	or 5 years of prior analytical experience
Spectra Interpretation	A college degree in an applied science or 2 years of college chemistry	And 2 years relevant experience Or 5 years of prior analytical experience
Technical Managers – **General**	Bachelor's Degree in an applied science or engineering with 24 semester hours in chemistry An advanced (MS, PhD.) degree may substitute for one year of experience	And 2 years experience in environmental analysis of representative analytes for which they will oversee
Technical Managers – Wet Chem only (no advanced instrumentation)	Associates degree in an applied science or engineering or 2 years of college with 16 semester hours in chemistry	And 2 years relevant experience

When an analyst does not meet these requirements, they can perform a task under the direct supervision of a qualified analyst, peer reviewer or Technical Manager, and are considered an analyst in training. The person supervising an analyst in training is accountable for the quality of the analytical data and must review and approve data and associated corrective actions.

3.3) Training

The laboratory is committed to furthering the professional and technical development of employees at all levels.

Orientation to the laboratory's policies and procedures, in-house method training, and employee attendance at outside training courses and conferences all contribute toward employee proficiency. Below are examples of various areas of required employee training:

Required Training	Time Frame	Employee Type
Environmental Health & Safety	Prior to lab work	All
Ethics – New Hires	1 week of hire	All
Ethics – Comprehensive	60 days of hire	All
Data Integrity	60 days of hire	Technical and PMs
Quality Assurance	90 days of hire	All
Ethics – Comprehensive Refresher	Annually	All
Initial Demonstration of Capability (DOC)	Prior to unsupervised method performance	Technical

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The laboratory maintains records of relevant authorization/competence, education, professional qualifications, training, skills and experience of technical personnel (including contracted personnel) as well as the date that approval/authorization was given. These records are kept on file at the laboratory. Also refer to "Demonstration of Capability" in Section 19.

The training of technical staff is kept up to date by:

- Each employee must have documentation in their training file that they have read, understood and agreed to follow the most recent version of the laboratory QA Manual and SOPs in their area of responsibility. This documentation is updated as SOPs are updated.
- Documentation from any training courses or workshops on specific equipment, analytical techniques or other relevant topics.
- Documentation of proficiency (refer to Section 19).
- An Ethics Agreement signed by each staff member (renewed each year) and evidence of annual ethics training.
- A Confidentiality Agreement signed by each staff member signed at the time of employment.
- Human Resources maintains documentation and attestation forms on employment status and records; benefit programs; timekeeping/payroll; and employee conduct (e.g., ethics violations). This information is maintained in the employee's secured personnel file.

Evidence of successful training could include such items as:

- Adequate documentation of training within operational areas, including one-on-one technical training for individual technologies, and particularly for people cross-trained.
- Analysts knowledge to refer to QA Manual for quality issues.
- Analysts following SOPs, i.e., practice matches SOPs.
- Analysts regularly communicate to supervisors and QA if SOPs need revision, rather than waiting for auditors to find problems.

Further details of the laboratory's training program are described in the Laboratory Training SOP (*EFGS-Q-QD-SOP2814*).

3.4) Data Integrity and Ethics Training Program

The laboratory's Ethics and Data Integrity Program is discussed in Section 5.2. Employees are trained as to the legal and environmental repercussions that result from data misrepresentation. Key topics covered in the presentation include:

- Organizational mission and its relationship to the critical need for honesty and full disclosure in all analytical reporting.
- Ethics Policy
- How and when to report ethical/data integrity issues. Confidential reporting.
- Record keeping.
- Discussion regarding data integrity procedures.
- Specific examples of breaches of ethical behavior (e.g. peak shaving, altering data or computer clocks, improper macros, etc., accepting/offering kickbacks, illegal accounting practices, unfair competition/collusion)
- Internal monitoring. Investigations and data recalls.
- Consequences for infractions including potential for immediate termination, debarment, or criminal prosecution.
- Importance of proper written narration / data qualification by the analyst and project manager with respect to those cases where the data may still be usable but are in one sense or another partially deficient.

Additionally, a data integrity hotline (1-800-736-9407) is maintained by the NDSC.

4) ACCOMMODATIONS AND ENVIRONMENTAL CONDITIONS

4.1) Overview

The laboratory is a 20,000 ft2 secure laboratory facility with controlled access and designed to accommodate an efficient workflow and to provide a safe and comfortable work environment for employees. All visitors sign in and are escorted by laboratory personnel. Access is controlled by various measures.

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The laboratory is equipped with structural safety features. Each employee is familiar with the location, use, and capabilities of general and specialized safety features associated with their workplace. The laboratory provides and requires the use of protective equipment including safety glasses, protective clothing, gloves, etc., OSHA and other regulatory agency guidelines regarding required amounts of bench and fume hood space, lighting, ventilation (temperature and humidity controlled), access, and safety equipment are met or exceeded.

Traffic flow through sample preparation and analysis areas is minimized to reduce the likelihood of contamination. Adequate floor space and bench top area is provided to allow unencumbered sample preparation and analysis space. Sufficient space is also provided for storage of reagents and media, glassware, and portable equipment. Ample space is also provided for refrigerated sample storage before analysis and archival storage of samples after analysis. Laboratory HVAC and deionized water systems are designed to minimize potential trace contaminants.

The laboratory is separated into specific areas for sample receiving, sample preparation, volatile organic sample analysis, non-volatile organic sample analysis, metals sample analysis and administrative functions.

4.2) Environment

Laboratory accommodation, test areas, energy sources, and lighting are adequate to facilitate proper performance of tests. The facility is equipped with heating, ventilation, and air conditioning (HVAC) systems appropriate to the needs of environmental testing performed at this laboratory.

The environment in which these activities are undertaken does not invalidate the results or adversely affect the required accuracy of any measurements.

The laboratory provides for the effective monitoring, control and recording of environmental conditions that may affect the results of environmental tests as required by the relevant specifications, methods, and procedures.

When any of the method or regulatory required environmental conditions change to a point where they may adversely affect test results, analytical testing will be discontinued until the environmental conditions are returned to the required levels.

Environmental conditions of the facility housing the computer network and LIMS are regulated to protect against raw data loss.

When the laboratory performs laboratory activities at sites or facilities outside its permanent control, it shall ensure that the requirements related to facilities and environmental conditions of this document are met.

Specific requirements for facility and environmental conditions, as well as periodic monitoring of conditions, are given in the Environmental Health & Safety Manual plus each laboratory’s Facility Addendum.

4.3) Work Areas

There is effective separation between neighboring areas when the activities therein are incompatible with each other. An example includes:

- Volatile organic chemical handling areas, including sample preparation and waste disposal, and volatile organic chemical analysis areas.

Access to and use of all areas affecting the quality of analytical testing is defined and controlled by secure access to the laboratory building as described below in the Building Security section.

Adequate measures are taken to ensure good housekeeping in the laboratory and to ensure that any contamination does not adversely affect data quality. These measures include regular cleaning to control dirt and dust within the laboratory. Work areas are available to ensure an unencumbered work area. Work areas include:

- Access and entryways to the laboratory.
- Sample receipt areas.
- Sample storage areas.

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- Chemical and waste storage areas.
- Data handling and storage areas.
- Sample processing areas.
- Sample analysis areas.

4.4) Responding to Emergencies

Employees must be aware of procedures to respond to all emergencies that might occur in the workplace. Employees must be familiar with the location and proper operation of all emergency equipment, evacuation routes and designated assembly areas for all areas where they work. Refer to the Chemical Hygiene Plan Document No. *EFGS-S-HS-12066*, Sec. 1.11 and the laboratory's Health and Safety Evaluation and Auditing, SOP No. *EFGS-S-HS-SOP5670* for complete details. These documents provide direction for situations where normal operations of the laboratory are not possible (e.g., electrical failures, heating/air conditioning failures, fire/building evacuation, computer failures, hazardous material spills, injury to employees, pandemic flu, disruption of phone service, etc.)

In the event that the building or information technology (IT) systems would be severely challenged, a designated disaster recovery team, which includes Facility Management, Maintenance, Safety, Laboratory/Executive Management, Public Relations, IT, QA and other applicable personnel depending on the scope of the disaster, would assemble at a designated area to assess the situation and formulate a plan.

4.5) Building Security

The laboratory is considered a secure facility. All outside doors are locked during normal business hours to prevent unauthorized entry. Building keys are distributed to employees as necessary.

All visitors to the laboratory must sign in and out in a visitor's logbook that is located in the lobby. A visitor is defined as any person who visits the laboratory who is not an employee of the laboratory. Both visitors and vendors must review and sign specific EH&S forms; and are escorted by laboratory personnel at all times, or the location of the visitor is noted in the visitor's logbook.

5) QUALITY SYSTEM

5.1) Quality Policy Statement

The Quality Policy statement gives employees clear requirements for the production of analytical data. As an organization, all personnel are committed to high quality professional practice, testing and data, and service to our clients.

We strive to provide the highest quality data achievable by:

- Reading and understanding all of the quality documents applicable to each position and implementing the process in our work.
- Following all recordkeeping requirements; describing clearly and accurately all activities performed; recording "real time" as the task is carried out; understanding that it is never acceptable to "back date" entries and should additional information be required at a later date, the actual date and by whom the notation is made must be documented.
- Ensuring data integrity through the completeness, consistency, impartiality and accuracy of the data generated. Data is attributable, legible, contemporaneously recorded, original or a true copy, and accurate (ALCOA). This applies to manual paper documentation and electronic records.
- Providing accountability and traceability for each sample analyzed through proper sample handling, labeling, preparation, instrument calibration/qualification/validation, analysis, and reporting; establishing an audit trail (the who, what, when, and why) that identifies date, time, analyst, instrument used, instrument conditions, quality control samples (where appropriate and/or required by the method), and associated standard material.
- Emphasizing a total quality management process which provides impartiality, accuracy, and strict compliance with agency regulations and client requirements, giving the highest degree of confidence; understanding that meeting the requirements of the next employee in the work flow process is just as important as meeting the needs of the external client.
- Providing thorough documentation and explanation to qualify reported data that may not meet all requirements and specifications, but is still of use to the client; understanding this occurs only after discussion with the client on the data limitations and acceptability of this approach.

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- Responding immediately to indications of questionable data, out-of-specification occurrences, equipment malfunctions, and other types of laboratory problems, with investigation and applicable corrective action; documenting these activities completely, including the reasons for the decisions made.
- Providing a work environment that ensures accessibility to all levels of management and encourages questions and expression of concerns on quality issues to management. Eurofins recognizes that the implementation of a quality assurance program requires management's commitment and support as well as the involvement of the entire staff
- Continually improve systems and manage risk to support quality improvement efforts in laboratory, administrative and managerial activities

5.2) Ethics and Data Integrity

Eurofins Environment Testing America is committed to ensuring the integrity of its data and meeting the quality needs of its clients. The laboratory operates our Ethics and Data Integrity program under the guidance of Eurofins Key Guidance Document (KGD). The elements of the our program include:

- An Ethics Policy (NDSC Document No. CW-L-P-004) and Employee Ethics Statements.
- Ethics and Compliance Officer/s (ECOs).
- A Training Program.
- Self-governance through disciplinary action for violations.
- A confidential mechanism for anonymously reporting alleged misconduct and a means for conducting internal investigations of all alleged misconduct. (NDSC Document No. CW-L-S-002).
- Procedures and guidance for recalling data if necessary (NDSC Document No. CW-Q-S-005).
- Effective external and internal monitoring system that includes procedures for internal audits (SOP No. *EFGS-Q-QD-SOP2989*).
- Produce results, which are accurate and include QA/QC information that meets client pre-defined Data Quality Objectives (DQOs).
- Present services in a confidential, honest and forthright manner.
- Provide employees with guidelines and an understanding of the Ethical and Quality Standards of our Industry.
- Provide procedures and guidance to ensure the impartiality and confidentiality of all data and customer information.
- Operate our facilities in a manner that protects the environment and the health and safety of employees and the public.
- Obey all pertinent federal, state and local laws and regulations and encourage other members of our industry to do the same.
- Educate clients as to the extent and kinds of services available.
- Assert competency only for work for which adequate personnel and equipment are available and for which adequate preparation has been made.
- Promote the status of environmental laboratories, their employees, and the value of services rendered by them.

5.3) Quality System Documentation

The laboratory's Quality System is communicated through a variety of documents.

- Quality Assurance (QA) Manual – Each laboratory has a lab-specific QA manual.
- NDSC Official Documents – Each laboratory may use the Guidance (instructional use) documents at their discretion. Template documents are process documents that the laboratory's need to implement locally by using the document as is or as an outline to define their internal practices that meet the minimum requirements of the template. Required documents need to be implemented as is and listed in the laboratory's document control list.
- Key Guidance Documents (KGDs) - Documents compiled at the Group Service Centre (GSC) level by Functional Leaders (document owners) aimed at providing specific Eurofins groups of employees with guidelines necessary for the good conduct of their respective work.
- Laboratory SOPs and Policies – General and Technical
- Work Instructions – A subset of procedural steps, tasks or forms associated with an operation of a management system (e.g., checklists, preformatted bench sheets, forms).

5.3.1) Order of Precedence

In the event of a conflict or discrepancy between policies, the order of precedence is as follows:

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- Quality Management Plan (QMP)
- NDSC Guidance Documents
- KGDs
- Laboratory Quality Assurance Manual (QA Manual)
- Laboratory SOPs and Policies
- Other (Work Instructions (WI), memos, flow charts, etc.)

Note: The laboratory has the responsibility and authority to operate in compliance with regulatory requirements of the jurisdiction in which the work is performed. Where the QMP conflicts with those regulatory requirements, the regulatory requirements of the jurisdiction shall hold primacy. The laboratory's QA Manual shall take precedence over the QMP in those cases.

5.4) QA/QC Objectives for the Measurement of Data

Quality Assurance (QA) is responsible for developing planned activities whose purpose is to provide assurance to all levels of management that a quality program is in place within the laboratory, and that it is functioning in an effective manner that is consistent with the requirements of NELAP, ISO 17025, DoD, DOE and any other regulatory agencies (i.e., states) in which the laboratory maintains accreditation.

Quality Control (QC) is generally understood to be limited to the analyses of samples and to be synonymous with the term *"analytical quality control"*. QC refers to the routine application of statistically based procedures to evaluate and control the accuracy of results from analytical measurements. The QC program includes procedures for estimating and controlling precision and bias and for determining reporting limits.

Request for Proposals (RFPs) and Quality Assurance Project Plans (QAPP) provide a mechanism for the client and the laboratory to discuss the data quality objectives in order to ensure that analytical services closely correspond to client needs. In order to ensure the ability of the laboratory to meet the Data Quality Objectives (DQOs) specified in the QAPP, clients are advised to allow time for the laboratory to review the QAPP before being finalized. The client is responsible for developing the QAPP; however, the laboratory will provide support to the client for developing the sections of the QAPP that concern laboratory activities.

Historically, laboratories have described their QC objectives in terms of precision, accuracy, representativeness, comparability, completeness, selectivity and sensitivity (PARCCSS). Each laboratory SOP defines the required QC indicators.

5.4.1) Precision

The objective is to meet the performance for precision demonstrated for the methods on similar samples and to meet DQOs of the EPA and/or other regulatory programs. Precision is defined as the degree of reproducibility of measurements under a given set of analytical conditions (exclusive of field sampling variability). Precision is documented on the basis of replicate analysis, usually duplicate or matrix spike (MS) duplicate samples.

5.4.2) Accuracy

The objective is to meet the performance for accuracy demonstrated for the methods on similar samples and to meet DQOs of the EPA and/or other regulatory programs. Accuracy is defined as the degree of bias in a measurement system. Accuracy may be documented through the use of laboratory control samples (LCS) and/or MS. A statement of accuracy is expressed as an interval of acceptance recovery about the mean recovery.

5.4.3) Representativeness

The objective is to provide data which is representative of the sampled medium. Representativeness is defined as the degree to which data represent a characteristic of a population or set of samples and is a measurement of both analytical and field sampling precision. The representativeness of the analytical data is a function of the procedures used in procuring and processing the samples. The representativeness can be documented by the relative percent difference between separately procured, but otherwise identical samples or sample aliquots.

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The representativeness of the data from the sampling sites depends on both the sampling procedures and the analytical procedures. Refer to laboratory SOPs for subsampling and homogenization techniques appropriate to the analytical method.

5.4.4) Comparability

The objective is to provide analytical data for which the accuracy, precision, representativeness, and reporting limit statistics are similar to these quality indicators generated by other laboratories for similar samples, and data generated by the laboratory over time.

Comparability is documented by inter-laboratory studies carried out by regulatory agencies or carried out for specific projects or contracts, by comparison of periodically generated statements of accuracy, precision, and reporting limits with those of other laboratories.

5.4.5) Completeness

The completeness objective for data is 90% (or as specified by a particular project), expressed as the ratio of the valid data to the total data over the course of the project. Data will be considered valid if they are adequate for their intended use. Data usability will be defined in a QAPP, project scope, or regulatory requirement. Data validation is the process for reviewing data to determine its usability and completeness. If the completeness objective is not met, actions will be taken internally and with the data user to improve performance. This may take the form of an audit to evaluate the methodology and procedures as possible sources for the difficulty or may result in a recommendation to use a different method.

5.4.6) Selectivity

Selectivity is defined as the capability of a test method or instrument to respond to a target substance or constituent in the presence of non-target substances. Target analytes are separated from non-target constituents and subsequently identified/detected through one or more of the following, depending on the analytical method: extractions (separation), digestions (separation), interelement corrections (separation), use of matrix modifiers (separation), specific retention times (separation and identification), confirmations with different columns or detectors (separation and identification), specific wavelengths (identification), specific mass spectra (identification), and specific electrodes (separation and identification).

5.4.7) Sensitivity

Sensitivity refers to the amount of analyte necessary to produce a detector response that can be reliably detected (above the Method Detection Limit) or quantified (above the Reporting Limit).

5.5) Criteria for Quality Indicators

The laboratory maintains tables, housed in LIMS, that summarize the precision and accuracy acceptability limits for performed analyses. This summary includes an effective date, is updated each time new limits are generated, and are managed by the laboratory's QA department. Unless otherwise noted, limits within these tables are laboratory generated. Some acceptability limits are derived from US EPA methods when they are required. Where US EPA method limits are not required, the laboratory has developed limits from evaluation of data from similar matrices. Criteria for development of control limits is contained in the Control Charting SOP No. *EFGS-Q-QD-SOP2819*.

5.6) Statistical Quality Control

Statistically-derived precision and accuracy limits are required by selected methods (such as SW-846) and programs. The laboratory routinely utilizes statistically-derived limits to evaluate method performance and determine when corrective action is appropriate. The analysts use the current limits entered into LIMS. The QA department maintains an archive of all limits used within the laboratory. If a method defines the QC limits, the method limits are used.

If a method requires the generation of historical limits, the lab develops such limits from recent data in the QC database of the LIMS following the guidelines described in Section 26. All calculations and limits are documented and dated when approved and effective. On occasion, a client requests contract-specified limits for a specific project.

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Current QC limits are entered and maintained in the LIMS analyte database. As sample results and the related QC are entered into LIMS, the sample QC values are compared with the limits in LIMS to determine if they are within the acceptable range. The analyst then evaluates if the sample needs to be rerun or re-extracted/rerun or if a comment should be added to the report explaining the reason for the QC outlier.

5.6.1) QC Charts

The QA Manager evaluates these to determine if adjustments need to be made or for corrective actions to methods. All findings are documented and kept on file. Further details of the laboratory's control charting program are described in the Laboratory Control Charting SOP (*EFGS-Q-QD-SOP2819*)

5.7) Quality System Metrics

In addition to the QC parameters discussed above, the entire Quality System is evaluated on a monthly basis through the use of specific metrics (refer to Section 16). These metrics are used to drive continuous improvement in the laboratory's Quality System.

6) DOCUMENT CONTROL

6.1) Overview

The QA Department is responsible for the control of documents used in the laboratory to ensure that approved, up-to-date documents are in circulation and out-of-date (obsolete) documents are archived or destroyed. The following documents, at a minimum, must be controlled:

- Laboratory Quality Assurance (QA) Manual
- Laboratory Standard Operating Procedures (SOP)
- Laboratory Policies
- Work Instructions and Forms
- NDSC Documents[1]
- KGDs[1]

[1]Includes locally implemented documents that are document controlled within the laboratory's document control system. The NDSC documents are only considered controlled when they are read on the intranet site. Printed copies are considered uncontrolled unless the laboratory physically distributes them as controlled documents. A detailed description of the procedure for issuing, authorizing, controlling, distributing, and archiving NDSC Official Documents is found in Document No. CW-Q-S-001, NDSC Document Control and Archiving. The laboratory's internal document control procedure is defined in SOP No. *EFGS-Q-QD-SOP2804*.

The laboratory QA Department also maintains access to various references and document sources integral to the operation of the laboratory. This includes reference methods and regulations. Instrument manuals (hard or electronic copies) are also maintained by the laboratory.

The laboratory maintains control of records for raw analytical data and supporting records such as audit reports and responses, logbooks, standard logs, training files, MDL studies, Proficiency Testing (PT) studies, certifications and related correspondence, and corrective action reports. Raw analytical data consists of bound logbooks, instrument printouts, any other notes, magnetic media, electronic data, and final reports.

6.2) Document Approval and Issue

The pertinent elements of the document control system includes a unique document title and number, pagination, the total number of pages of the item or an 'end of document' page, the effective date, revision number, and the laboratory's name. The QA personnel are responsible for the maintenance of this system.

Controlled documents are authorized by the QA Department. In order to develop a new document, a responsible manager submits an electronic draft to the QA Department for suggestions and approval before use. Upon approval, QA personnel add the identifying version information to the document and retains that document as the official document on file. That document is then provided to all applicable operational units. Controlled documents are identified as such and records of their

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distribution are kept by the QA Department. Document control may be achieved by either electronic or hardcopy distribution.

The QA Department maintains a list of the official versions of controlled documents.

Quality System Policies and Procedures will be reviewed at a minimum of every year and revised as appropriate. Changes to documents occur when a procedural change warrants.

6.3) Procedures for Document Control Policy

Changes to the QA Manual are tracked by revision number. Whenever practical, altered or new text shall be italicized in the document. Uncontrolled copies must not be used within the laboratory. Previous revisions and back-up data are stored by the QA department. Electronic copies are stored on the Public server in the QA folder (or define location) for the applicable revision.

For changes to SOPs, refer to Document No. *EFGS-Q-QD-SOP2804*, (Creation and Control of Standard Operating Procedures). The SOP identified above also defines the process of changes to SOPs.

Forms, worksheets, work instructions and information are organized by department in the QA office. There is a table of contents. Electronic versions are kept on a hard drive in the QA department; hard copies are kept in QA files.

6.4) Obsolete Documents

All invalid or obsolete documents are removed, or otherwise prevented from unintended use. The laboratory has specific procedures as described above to accomplish this. In general, obsolete documents are collected from employees according to distribution lists and are marked obsolete on the cover or destroyed. At least one copy of the obsolete document is archived according to SOP No. *EFGS-Q-QD-SOP2804*.

7) SERVICE TO THE CLIENT

7.1) Overview

The laboratory has established procedures for the review of work requests and contracts, oral or written. The procedures include evaluation of the laboratory's capability and resources to meet the contract's requirements within the requested time period. All requirements, including the methods to be used, must be adequately defined, documented and understood. For many environmental sampling and analysis programs, testing design is site or program specific and does not necessarily fit into a standard laboratory service or product. It is the laboratory's intent to provide both standard and customized environmental laboratory services to our clients.

A thorough review of technical and QC requirements contained in contracts is performed to ensure project success. The appropriateness of requested methods, and the lab's capability to perform them must be established. Projects, proposals, and contracts are reviewed for adequately defined requirements and the laboratory's capability to meet those requirements. Alternate test methods that are capable of meeting the clients' requirements may be proposed by the lab. A review of the lab's capability to analyze non-routine analytes is also part of this review process.

All projects, proposals and contracts are reviewed for the client's requirements in terms of compound lists, test methodology requested, sensitivity (detection and reporting levels), accuracy, and precision requirements (% Recovery and RPD). The reviewer ensures that the laboratory's test methods are suitable to achieve these requirements and that the laboratory holds the appropriate certifications and approvals to perform the work. The laboratory and any potential subcontract laboratories must be certified, as required, for all proposed tests.
Electronic or hard copy deliverable requirements are evaluated against the laboratory's capacity for production of the documentation.

If the laboratory cannot provide all services but intends to subcontract such services, whether to another Eurofins facility on the same LIMS or to an outside firm, this will be documented and discussed with the client prior to contract approval. (Refer to Section 10 for Subcontracting Procedures.)

The laboratory informs the client of the results of the review if it indicates any potential conflict, deficiency, lack of accreditation, or inability of the lab to complete the work satisfactorily. Any

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discrepancy between the client's requirements and the laboratory's capability to meet those requirements is resolved in writing before acceptance of the contract. It is necessary that the contract be acceptable to both the laboratory and the client. Amendments initiated by the client and/or Eurofins Seattle are documented in writing.

All contracts, QAPPs, Sampling and Analysis Plans (SAPs), contract amendments, and documented communications become part of the project record.

The same contract review process used for the initial review is repeated when there are amendments to the original contract by the client, and the participating personnel are informed of the changes.

7.2) Review Sequence and Key Personnel

Appropriate personnel will review the work request at each stage of evaluation.

For routine projects and other simple tasks, a review by the Project Manager (PM) is considered adequate. The PM confirms that the laboratory has any required certifications, that it can meet the clients' data quality and reporting requirements and that the lab has the capacity to meet the clients turn around needs. It is recommended that, where there is a sales person assigned to the account, an attempt should be made to contact that sales person to inform them of the incoming samples.

For new, complex or large projects, the proposed contract is given to the Client Relationship Manager or Proposal Team, who will decide which lab will receive the work based on the scope of work and other requirements, including certification, testing methodology, and available capacity to perform the work. The contract review process is outlined in NDSC Document No. CA-L-P-002, Contract Compliance Policy or define local SOP No. *EFGS-P-PM-SOP2815* "Contract Review".

This review encompasses all facets of the operation. The scope of work is distributed to the appropriate personnel, as needed based on scope of contract, to evaluate all of the requirements shown above (not necessarily in the order below):

- Laboratory Project Manager
- BUMA and/or Technical Managers
- Account Executives
- Quality Managers
- Laboratory Environmental Health and Safety Managers/Directors

The BUMA reviews the formal laboratory quote and makes final acceptance for their facility.

The Sales Director, Contract Administrator, Account Executive or Proposal Coordinator then submits the final proposal to the client.

In the event that one of the above personnel is not available to review the contract, his or her back-up will fulfill the review requirements.

7.3) Balancing Laboratory Capacity and Workload

Evaluating laboratory capacity to perform specific projects is the responsibility of the Vice-President, Laboratory Director/BUMA and Managers. Many analysts are cross-trained to perform a variety of tests, and there is redundant equipment available in case of malfunctions. This minimizes the need to evaluate small and medium size projects against capacity available to complete them. Large and complex projects are reviewed against capacity estimates before bids are submitted to ensure that the client's analysis schedule is met. Regularly scheduled meetings are held between laboratory management, PMs and QA personnel to review progress with current projects, as well as special requirements of new work scheduled for the laboratory. Laboratory capacity and backlog is tracked on a continuous basis using information from the Laboratory Sample Information System (LIMS) including turnaround time, and work in-house.

7.4) Documentation

The Contracts Department and the Laboratory Director/BUMA maintain copies of all signed contracts.

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Appropriate records are maintained for every contract or work request. All stages of the contract review process are documented and include records of any significant changes. Appropriate records are maintained for every contract or work request in the contract directory on the server.

The contract will be distributed to and maintained by the appropriate sales/marketing personnel and the Account Executive. A copy of the contract and formal quote will be filed with the laboratory PM and the Laboratory Director/BUMA.

Records are maintained of pertinent discussions with a client relating to the client's requirements or the results of the work during the period of execution of the contract. The PM keeps a phone log of conversations with the client and officially documented with a follow-up email to the client.

7.4.1) Project-Specific Quality Planning

Communication of contract specific technical and QC criteria is an essential activity in ensuring the success of site specific testing programs. To achieve this goal, a PM is assigned to each client. It is the PM's responsibility to ensure that project-specific technical and QC requirements are effectively evaluated and communicated to the laboratory personnel before and during the project. QA department involvement may be needed to assist in the evaluation of custom QC requirements. PM's are the primary client contact and they ensure resources are available to meet project requirements, they coordinate opportunities and work with laboratory management and supervisory staff to ensure available resources are sufficient to perform work for the client's project.

Prior to work on a new project, the dissemination of project information and/or project opening meetings may occur to discuss schedules and unique aspects of the project. Items to be discussed may include the project technical profile, turnaround times, holding times, methods, analyte lists, reporting limits, deliverables, sample hazards, or other special requirements. The PM introduces new project information to maximize production and client satisfaction, while maintaining quality.

Any change that may occur within an active project is agreed upon between the client/regulatory agency and the PM/laboratory. These changes (e.g., use of a non-standard method or modification of a method) and approvals must be documented prior to implementation. Documentation pertains to any document (e.g., letter, e-mail, variance, contract addendum), which has been signed by both parties.

Such changes are also communicated to the laboratory via e-mail. The laboratory staff is then introduced to the modified requirements via the PM or the individual laboratory Technical Manager. After the modification is implemented into the laboratory process, documentation of the modification is made in the case narrative of the data report(s).

The laboratory strongly encourages client visits to the laboratory and for formal/informal information sharing session with employees in order to effectively communicate ongoing client needs as well as project specific details for customized testing programs.

7.5) Special Services

The laboratory cooperates with clients and their representatives to monitor the laboratory's performance in relation to work performed for the client. It is the laboratory's goal to meet all client requirements in addition to statutory and regulatory requirements. The laboratory has procedures to ensure confidentiality to clients (Section 15 and 23).

The laboratory's standard procedures for reporting data are described in Section 23. Special services are also available and provided upon request. These services include:

- Reasonable access for our clients or their representatives to the relevant areas of the laboratory for the witnessing of tests performed for the client.
- Assisting client-specified third party data validators as specified in the client's contract.
- Supplemental information pertaining to the analysis of their samples. Note: An additional charge may apply for additional data/information that was not requested prior to the time of sample analysis or previously agreed upon.

When the client requests a statement of conformity to a specification or standard based on the analysis performed by the laboratory (e.g., pass/fail, in-tolerance/out-of-tolerance), the decision rule shall be clearly defined. Unless inherent in the requested specification or standard, the decision rule

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selected shall be communicated to the client. Associated reporting requirements are addressed in Section 23.2.18.

7.6) Client Communication

PMs are the primary communication link to the clients. They shall inform their clients of any delays in project completion as well as any non-conformances in either sample receipt or sample analysis. Project management will maintain ongoing client communication throughout the entire client project.

Technical Managers are available to discuss any technical questions or concerns that the client may have.

7.7) Reporting

The laboratory works with our clients to produce any special communication reports required by the contract.

7.8) Client Feedback and Surveys

The laboratory assesses both positive and negative client feedback. The results are used to improve overall laboratory quality and client service. Eurofins Sales and Marketing teams periodically develop lab and client specific surveys to assess client satisfaction.

When a complaint is received, we determine, to the best of our ability, the extent of the issue and what data is in question. The person receiving the complaint documents this information and promptly forwards it to the appropriate management personnel where the work in question was performed. If a data reporting error is discovered, the final report and/or data must be regenerated with the correct value(s).

The Quality Assuance Manager is responsible for entering client concerns into iCAT. In some cases, an iCAT / ICAR (Investigation and Corrective Action Report) is initiated to address and document the situation. While an individual issue may not warrant a formal investigation, QA monitors these issues for potential trends and will issue an iCAT/ICAR if a trend is evident.

8) SUBCONTRACTING OF TESTS

The laboratory may subcontract tests to other laboratories if the requested testing is not routinely performed in our laboratory. To a lesser extent, samples may need to be subcontracted to an overflow laboratory to ensure hold times and/or turn-around-times (TAT) are met.

Testing is only subcontracted with the client's knowledge and approval. The PM must notify the client in writing when any of their requested analyses will be subcontracted to another lab. Client approval must be obtained in writing before samples are shipped.

Subcontract laboratories are selected based on their qualifications and accreditations. The subcontractor is requested to sign a Laboratory Analytical Services Subcontract. See form Q-EQA-FRM6867 to review details of the contract terms and information requested from the subcontract laboratory. If projects require a specific agency certification (i.e. individual state agencies, NELAP, DoD, ISO 17025), only an appropriately accredited laboratory is used. The client may also have a list of laboratories to be used for subcontracting. In these cases, the evaluation of the subcontract laboratory is made by the client.

Data obtained from subcontract laboratories is clearly marked as such when reported by the laboratory. The data are submitted to the client in the format obtained from the subcontractor.

8.1) Overview

For the purpose of this quality manual, the phrase subcontract laboratory refers to a laboratory external to the Eurofins Environment Testing America laboratories. The phrase "work sharing" refers to internal transfers of samples between the Eurofins Environment Testing America laboratories. The term outsourcing refers to the act of subcontracting tests.

When contracting with our clients, the laboratory makes commitments regarding the services to be performed and the data quality for the results to be generated. When the need arises to outsource

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testing for our clients because project scope, changes in laboratory capabilities, capacity, or unforeseen circumstances, we must be assured that the subcontractors or work sharing laboratories understand the requirements and will meet the same commitments we have made to the client. Refer to the NDSC Documents on Subcontracting Procedures (CW-L-S-004) and the Work Sharing Process (CA-C-S-001) and SOP *EFGS-P-PM-SOP40740*, Subcontracting Samples.

When outsourcing analytical services, the laboratory will assure, to the extent necessary, that the subcontract or work sharing laboratory maintains a program consistent with the requirements of this document, the requirements specified in TNI/ISO 17025 and/or the client's Quality Assurance Project Plan (QAPP). All QC guidelines specific to the client's analytical program are transmitted to the subcontractor and agreed upon before sending the samples to the subcontract facility. Additionally, work requiring accreditation will be placed with an appropriately accredited laboratory. The laboratory performing the subcontracted work will be identified in the final report, as will non-TNI accredited work where required.

PMs or other responsible Client Service members, for the Export Lab (i.e., the Eurofins Environment Testing America laboratory that transfers samples to another laboratory) are responsible for obtaining client approval prior to subcontracting any samples. The laboratory will advise the client of a subcontract arrangement in writing and when possible approval from the client shall be obtained and retained in the project folder. Standard Eurofins Seattle Terms & Conditions include the flexibility to subcontract samples within the Eurofins Environment Testing America laboratories. Therefore, additional advance notification to clients for intra-laboratory subcontracting is not necessary unless specifically required by a client contract.

Note: In addition to the client, some regulating agencies (e.g., USDA) or contracts (e.g., DoD and DOE projects) require notification prior to placing such work.

8.2) Qualifying and Monitoring Subcontractors

Whenever a PM [or Account Executive (AE), etc.] becomes aware of a client requirement or laboratory need where samples must be outsourced to another laboratory, the other laboratory(s) shall be selected based on the following:

- Subcontractors specified by the client - In these circumstances, the client assumes responsibility for the quality of the data generated from the use of a subcontractor.
- Subcontractors reviewed by Eurofins Seattle – Firms which have been reviewed by the company and are known to meet standards for accreditations (e.g., State, TNI and DoD/DOE); technical specifications; legal and financial information.
- A listing of vendors is available on the public drive; \\TAFS\Lab\Seattle\Public\Proposals\Subcontract_Lab_Approval.

All Eurofins Environmental Testing America laboratories are pre-qualified for work sharing provided they hold the appropriate accreditations and can adhere to the project/program requirements. Client approval is not necessary unless specifically required by the contract. In these cases, the client must provide acknowledgement that the samples can be sent to that facility (an e-mail is sufficient documentation or if acknowledgement is verbal, the date, time, and name of person providing acknowledgement must be documented). The originating laboratory is responsible for communicating all technical, quality, and deliverable requirements as well as other contract needs. (NDSC Document No. CA-C-S-001, Work Sharing Process).

8.2.1 When the potential subcontract laboratory has not been previously approved, Account Executives or PMs may nominate a laboratory as a subcontractor based on need. The decision to nominate a laboratory must be approved by the Laboratory Director/BUMA. The Laboratory Director/BUMA requests that the QA Manager begin the process of approving the subcontract laboratory.

Once the appropriate accreditation and legal information is received by the laboratory, it is evaluated for acceptability and forwarded to the Finance Department for formal signature and contracting with the laboratory. The approved vendor will be added to the approved subcontractor list on the public drive.

The client will assume responsibility for the quality of the data generated from the use of a subcontractor they have requested the lab to use. The qualified subcontractors on the public drive

site are known to meet minimal standards. Eurofins Seattle does not certify laboratories. The subcontractors on our approved list can only be recommended to the extent that we would use them.

8.3) Oversight and Reporting

The status and performance of qualified subcontractors will be monitored by the Quality Assurance Manager, and includes an annual review process (SOP No. *EFGS-S-P-SOP2809* "Ordering Laboratory Supplies/Services"). Any problems identified will be brought to the attention of the Laboratory Director/BUMA, Procurement personnel, etc.

- Complaints shall be investigated. Documentation of the complaint, investigation, and corrective action will be maintained in the subcontractor's file on the intranet site. Complaints are posted using the Vendor Performance Report.
- Information shall be updated on the intranet when new information is received from the subcontracted laboratories.
- Subcontractors in good standing will be retained on the approved subcontractor listing. Client Service personnel will notify the Quality Assurance Manager if any laboratory requires removal from the approved subcontractor list.

Prior to initially sending samples to the subcontracted laboratory, the PM confirms their certification status to determine if it's current and scope-inclusive. The information is documented within the project records.

The laboratory's certifications can be viewed on the company's website @ http://www.eurofinsus.com/

8.3.1 All subcontracted samples must be accompanied by a Eurofins Seattle's Chain of Custody (COC). A copy of the original COC sent by the client must be available in LIMS for all samples workshared. Client COCs are only forwarded to external subcontractors when samples are shipped directly from the project site to the subcontractor lab. Under routine circumstances, client COCs are not provided to external subcontractors.

Through communication with the subcontracted laboratory, the PM monitors the status of the subcontracted analyses, facilitates successful execution of the work, and ensures the timeliness and completeness of the analytical report.

Non-TNI accredited work must be identified in the subcontractor's report as appropriate. If TNI accreditation is not required, the report does not need to include this information.

Reports submitted from subcontractor laboratories are not altered and are included in their original form in the final project report. This clearly identifies the data as being produced by a subcontractor facility. If subcontract laboratory data is incorporated into the laboratory's EDD (i.e., imported), the report must explicitly indicate which lab produced the data for which methods and samples.

Note: The results submitted by a Eurofins Environment Testing work sharing laboratory may be transferred electronically and the results reported by the Eurofins Environment Testing work sharing lab are identified on the final report. The report must explicitly indicate which lab produced the data for which methods and samples. The final report must include a copy of the completed COC for all work sharing reports.

8.4) Contingency Planning

The full qualification of a subcontractor may be waived to meet emergency needs. This decision and justification must be documented in the project files, and the 'Purchase Order Terms And Conditions For Subcontracted Laboratory Services' must be sent with the samples and COC.

In the event this provision is utilized, the laboratory (e.g., PM) will be required to verify and document the applicable accreditations of the subcontractor. All other quality and accreditation requirements will still be applicable, but the subcontractor need not have signed a subcontract agreement with Eurofins Seattle at this time.

8.5) Use of NELAP and A2LA Logo

It is not laboratory policy to use these logos on any company letterhead, including analytical reports.

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9) PURCHASING SERVICES AND SUPPLIES

9.1) Overview

Evaluation and selection of suppliers and vendors is performed, in part, on the basis of the quality of their products, their ability to meet the demand for their products on a continuous and short term basis, the overall quality of their services, their past history, and competitive pricing. This is achieved through evaluation of objective evidence of quality furnished by the supplier, which can include certificates of analysis, recommendations, and proof of historical compliance with similar programs for other clients. To ensure that quality critical consumables and equipment conform to specified requirements, which may affect quality, all purchases from specific vendors are approved by a member of the supervisory or management staff.

Contracts will be signed in accordance with the laboratory's Authorization Matrix Policy**.** Request for Proposals (RFP's) will be issued where more information is required from the potential vendors than just price. Process details are available in the NDSC Document No. CW-F-P-004, Guidance on Procurement and Contracts Policy. RFP's allow the laboratory to determine if a vendor is capable of meeting requirements such as supplying all of the laboratory facilities, meeting required quality standards and adhering to necessary ethical and environmental standards. The RFP process also allows potential vendors to outline any additional capabilities they may offer.

9.2) Glassware

Glassware used for volumetric measurements must be Class A or verified for accuracy according to laboratory procedure. Pyrex (or equivalent) glass should be used where possible. For safety purposes, thick-wall glassware should be used where available.

9.3) Reagents, Standards & Supplies

Purchasing guidelines for equipment, consumables, and reagents must meet the requirements of the specific method and testing procedures for which they are being purchased. Solvents and acids are pre-tested in accordance with NDSC Document No. CA-Q-S-001, Solvent & Acid Lot Testing & Approval**.** Approval information for the solvents and acids tested under Document No. CA-Q-S-001 is stored on the Eurofin's SharePoint site, under Solvent Approvals. A master list of all tested materials, as well as the certificates of analysis for the materials, is stored in the same location.

9.3.1) Purchasing

Chemical reagents, solvents, glassware, and general supplies are ordered as needed to maintain sufficient quantities on hand. Materials used in the analytical process must be of a known quality. The wide variety of materials and reagents available makes it advisable to specify recommendations for the name, brand, and grade of materials to be used in any determination. This information is contained in the method SOP. The analyst completes the Material Request Sheet when requesting reagents, standards, or supplies.

The analyst must provide the master item number (from the master item list that has been approved by the Technical Manager), item description, package size, catalogue page number, and the quantity needed. If an item being ordered is not the exact item requested, approval must be obtained from the Technical Manager or Department Manager prior to placing the order. The purchasing manager or Department Manager places the order.

9.3.2) Receiving

It is the responsibility of the purchasing manager to receive the shipment. It is the responsibility of the analyst who ordered the materials to document the date materials were received. Once the ordered reagents or materials are received, the analyst compares the information on the label or packaging to the original order to ensure that the purchase meets the quality level specified. This is documented through the addition of the received date and initials to the information present on the daily order log.

The purchasing manager verifies the lot numbers of received solvents and acids against the pre-approval lists. If a received material is listed as unapproved, or is not listed, it is sequestered and returned to the vendor. Alternatively, the laboratory may test the material for the intended use, and if it is acceptable, document the approval on the approval list. Records of any testing performed locally are maintained on the shared "public" folder on the computer network.

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Materials may not be released for use in the laboratory until they have been inspected, verified as suitable for use, and the inspection/verification has been documented.

Safety Data Sheets (SDSs) are available online through the Company's intranet website. Anyone may review these for relevant information on the safe handling and emergency precautions of on-site chemicals.

9.3.3) Specifications

Methods used in the laboratory specify the grade of reagent that must be used in the procedure. If the quality of the reagent is not specified, analytical reagent grade will be used. It is the responsibility of the analyst to check the procedure carefully for the suitability of grade of reagent.

Chemicals must not be used past the manufacturer's expiration date and must not be used past the expiration time noted in a method SOP. If expiration dates are not provided, the laboratory may contact the manufacturer to determine an expiration date.

The laboratory assumes a five year expiration date on inorganic dry chemicals and solvents unless noted otherwise by the manufacturer or by the reference source method. Chemicals/solvents should not be used past the manufacturer's or SOP expiration date unless verified as outlined below.

- An expiration date **cannot** be extended if the dry chemical/solvent is discolored or appears otherwise physically degraded. In this case, the dry chemical/solvent must be discarded.
- Expiration dates can be extended if the dry chemical/solvent is found to be satisfactory based on acceptable performance of quality control samples (Continuing Calibration Verification (CCV), Blanks, Laboratory Control Sample (LCS), etc.).
- If the dry chemical/solvent is used for the preparation of standards, the expiration dates can be extended 6 months if the dry chemical/solvent is compared to an unexpired independent source in performing the method and the performance of the dry chemical/solvent is found to be satisfactory. The comparison must show that the dry chemical/solvent meets CCV limits. The comparison studies are maintained on-file and available for review in the reagent module of the LIMS.

Wherever possible, standards must be traceable to national or international standards of measurement or to national or international reference materials. Records to that effect are available to the user.

Compressed gases in use are checked for pressure and secure positioning daily. To prevent a tank from going to dryness, or introducing potential impurities, the pressure should be closely watched as it decreases to approximately 15% of the original reading, at which point it should be replaced. For example, a standard sized laboratory gas cylinder containing 3,000 psig of gas should be replaced when it drops to approximately 500 psig. The quality of the gases must meet method or manufacturer specification or be of a grade that does not cause any analytical interference.

Water used in the preparation of samples, standards or reagents must have a specific conductivity of less than 1-µmho/cm (or specific resistivity of greater than 1.0 megohm-cm) at 25°C. The specific conductivity is checked and recorded daily. If the water's specific conductivity is greater than the specified limit, the Facility Manager and appropriate Technical Managers must be notified immediately in order to notify all departments, decide on cessation (based on intended use) of activities, and make arrangements for correction.

The laboratory may purchase reagent grade (or other similar quality) water for use in the laboratory. This water must be certified clean by the supplier for all target analytes or otherwise verified by the laboratory prior to use. This verification is documented.

Standard lots are verified before first time use if the laboratory switches manufacturers or has historically had a problem with the type of standard.

Purchased bottleware used for sampling must be certified clean and the certificates must be maintained. If uncertified sampling bottleware is purchased, all lots must be verified clean prior to use. This verification must be maintained.

Records of manufacturer's certification and traceability statements are maintained in files. These records include date of receipt, lot number (when applicable), and expiration date (when

applicable). Incorporation of the item into the record indicates that the analyst has compared the new certificate with the previous one for the same purpose and that no difference is noted, unless approved and so documented by the Technical Manager or QA Manager.

9.3.4) Storage

Reagent and chemical storage is important from the aspects of both integrity and safety. Light-sensitive reagents may be stored in brown-glass containers. Storage conditions are per the Chemical Hygiene Plan Document No. *EFGS-S-HS-12066* and method SOPs or manufacturer instructions.

9.4) Purchase of Equipment / Instruments / Software

When a new piece of equipment is needed, either for additional capacity or for replacing inoperable equipment, the analyst or supervisor makes a supply request to the Technical Manager and/or the Laboratory Director/BUMA. If they agree with the request, the procedures outlined in NDSC Document No. CA-T-P-001**.** Qualified Products List, are followed. A decision is made as to which piece of equipment can best satisfy the requirements. The appropriate written requests are completed and purchasing places the order.

Upon receipt of a new or used piece of equipment, an identification name is assigned and added to the equipment list. IT must also be notified so that they can synchronize the instrument for back-ups. Its capability is assessed to determine if it is adequate or not for the specific application. For instruments, a calibration curve is generated, followed by MDLs, Demonstration of Capabilities (DOCs), and other relevant criteria (refer to Section 20). For software, its operation must be deemed reliable and evidence of instrument verification must be retained by the IT Department or QA Department. Software certificates supplied by the vendors are filed with the LIMS Administrator. The manufacturer's operation manual is retained at the bench.

9.5) Services

Service to analytical instruments (except analytical balances) is performed on an as needed basis. Routine preventative maintenance is discussed in Section 22. The need for service is determined by analysts and/or Technical Managers. The service providers that perform the services are approved by the Technical Manager.

Analytical balances are serviced and calibrated annually in accordance with SOP No. *EFGS-Q-QD-SOP2710*. The calibration and maintenance services are performed on-site, and the balances are returned to use immediately following successful calibration. Calibration certificates are filed for reference. If the calibration was unsuccessful, the balance is immediately removed from service and segregated pending either further maintenance or disposal.

Calibration services for support equipment such as thermometers, weight sets, autopipettors, etc., are obtained from vendors with current and valid ISO 17025 accreditation for calibration of the specific piece of equipment. Prior to utilizing the vendor's services, the vendor's accreditation status is verified. Once the equipment has been calibrated, the calibration certificates are reviewed by the QA department, and documentation of the review is filed with the calibration certificates. The equipment is then returned to service within the laboratory

9.6) Suppliers

The laboratory selects vendors through a competitive proposal / bid process, strategic business alliances or negotiated vendor partnerships (contracts).

This process is defined in the NDSC Document No. CW-F-P-004, Procurement & Contracts Policy and laboratory SOP *EFGS-S-P-SOP2809*, Ordering Laboratory Supplies. The level of control used in the selection process is dependent on the anticipated spending amount and the potential impact on the laboratory's business. Vendors that provide test and measuring equipment, solvents, standards, certified containers, instrument related service contracts or subcontract laboratory services shall be subject to more rigorous controls than vendors that provide off-the-shelf items of defined quality that meet the end use requirements. The purchasing system includes all suppliers/vendors that have been approved for use.

Evaluation of suppliers is accomplished by ensuring the supplier ships the product or material ordered and that the material is of the appropriate quality. This is documented by signing off on

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packing slips or other supply receipt documents. The purchasing documents contain the data that adequately describe the services and supplies ordered.

Any issues of vendor performance are to be reported immediately by the laboratory staff to the Purchasing Group by completing a Vendor Performance Report.

The Purchasing Group will work through the appropriate channels to gather the information required to clearly identify the problem and will contact the vendor to report the problem and to make any necessary arrangements for exchange, return authorization, credit, etc.

Suppliers are subject to re-evaluation, as deemed appropriate, through the use of Vendor Performance Reports used to summarize and review to determine corrective action necessary, or service improvements required by vendors

The laboratory has access to a listing of all approved suppliers of critical consumables, supplies and services. This information is provided through the purchasing system.

9.6.1) New Vendor Procedure

Laboratory employees who wish to request the addition of a new vendor must complete a Vendor Add Request Form.

New vendors are evaluated based upon criteria appropriate to the products or services provided as well as their ability to provide those products and services at a competitive cost. Vendors are also evaluated to determine if there are ethical reasons or potential conflicts of interest with laboratory employees that would make it prohibitive to do business with them as well as their financial stability. The QA Department and/or the Technical Services Director are consulted with vendor and product selection that have an impact on quality.

10) COMPLAINTS

10.1) Overview

The laboratory considers an effective client complaint handling processes to be of significant business and strategic value. Listening to and documenting client concerns captures client knowledge that enables our operations to continually improve processes and client satisfaction. An effective client complaint handling process also provides assurance to the data user that the laboratory will stand behind its data, service obligations and products.

A client complaint is any expression of dissatisfaction with any aspect of our business services (e.g., communications, responsiveness, data, reports, invoicing and other functions) expressed by any party, whether received verbally or in written form. Client inquiries, complaints or noted discrepancies are documented, communicated to management, and addressed promptly and thoroughly.

The laboratory has procedures for addressing both external and internal complaints with the goal of providing satisfactory resolution to complaints in a timely and professional manner.

The nature of the complaint is identified, documented and investigated, and an appropriate action is determined and taken. In cases where a client complaint indicates that an established policy or procedure was not followed, the QA Department must evaluate whether a special audit must be conducted to assist in resolving the issue. A written confirmation or letter to the client, outlining the issue and response taken is recommended as part of the overall action taken.

The process of complaint resolution and documentation utilizes the procedures outlined in Section 14 (Corrective Actions) and is documented following SOP *EFGS-Q-QD-SOP2835*. A copy of this procedure will be made available to any interested party on request.

10.2) External Complaints

An employee that receives a complaint initiates the complaint resolution process by first documenting the complaint according to (SOP# *EFGS-Q-QD-SOP2835*).

Complaints fall into two categories: correctable and non-correctable. An example of a correctable complaint would be one where a report re-issue would resolve the complaint. An example of a non-correctable complaint would be one where a client complains that their data was repeatedly late.

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Non-correctable complaints should be reviewed for preventive action measures to reduce the likelihood of future occurrence and mitigation of client impact.

The general steps in the complaint handling process are:

- Receiving and documenting complaints
- Acknowledging receipt of complaint, whenever possible
- Complaint investigation and service recovery
- Process improvement

The laboratory shall inform the initiator of the complaint of the results of the investigation and the corrective action taken, if any.

10.3) Internal Complaints

Internal complaints include, but are not limited to: errors and non-conformances, training issues, internal audit findings, and deviations from methods. Corrective actions may be initiated by any staff member who observes a nonconformance and shall follow the procedures outlined in Section 12. In addition, Executive Management, Sales and Marketing and IT may initiate a complaint by contacting the laboratory or through the corrective action system described in Section 12.

10.4) Management Review

The number and nature of client complaints is reported by the QA Manager to the Laboratory Director/BUMA and Quality Director in the QA Monthly report. Monitoring and addressing the overall level and nature of client complaints and the effectiveness of the solutions is part of the Annual Management Systems Review (Section 16).

11) CONTROL OF NON-CONFORMING WORK

11.1) Overview

When data discrepancies are discovered or deviations and departures from laboratory SOPs, policies and/or client requests have occurred, corrective action is taken immediately. First, the laboratory evaluates the significance of the nonconforming work. Then, a corrective action plan is initiated based on the outcome of the evaluation. If it is determined that the nonconforming work is an isolated incident, the plan could be as simple as adding a qualifier to the final results and/or making a notation in the case narrative. If it is determined that the nonconforming work is a systematic or improper practices issue, the corrective action plan could include a more in depth investigation and a possible suspension of an analytical method. In all cases, the actions taken are documented using the laboratory's corrective action system (refer to Section 12).

Due to the frequently unique nature of environmental samples, sometimes departures from documented policies and procedures are needed. When an analyst encounters such a situation, the problem is presented to the supervisor for resolution. The supervisor may elect to discuss it with the Technical Manager or have a representative contact the client to decide on a logical course of action. Once an approach is agreed upon, the analyst documents it using the laboratories corrective action system described in Section 12. This information can then be supplied to the client in the form of a footnote or a case narrative with the report.

Project Management may encounter situations where a client may request that a special procedure be applied to a sample that is not standard lab practice. Based on a technical evaluation, the lab may accept or opt to reject the request based on technical or ethical merit. An example might be the need to report a compound that the lab does not normally report. The lab would not have validated the method for this compound following the procedures in Section 19. The client may request that the compound be reported based only on the calibration. Such a request would need to be approved by the Technical Manager and QA Manager, documented and included in the project folder. Deviations must also be noted on the final report with a statement that the compound is not reported in compliance with TNI (or the analytical method) requirements and the reason. Data being reported to a non-TNI state would need to note the change made to how the method is normally run.

11.2) Responsibilities and Authorities

Under certain circumstances, the Laboratory Director/BUMA, a Technical Manager, or a member of the QA team may authorize departures from documented procedures or policies. The departures

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may be a result of procedural changes due to the nature of the sample; a one-time procedure for a client; QC failures with insufficient sample to reanalyze, etc. In most cases, the client will be informed of the departure prior to the reporting of the data. Any departures must be well documented using the laboratory's corrective action procedures. This information may also be documented in logbooks and/or data review checklists as appropriate. Any impacted data must be referenced in a case narrative and/or flagged with an appropriate data qualifier.

Any misrepresentation or possible misrepresentation of analytical data discovered by any laboratory staff member must be reported to facility Senior Management within 24-hours. The Senior Management staff is comprised of the Laboratory Director/BUMA, the QA Manager, and the Technical Managers. The reporting of issues involving alleged violations of the company's Data Integrity or Manual Integration procedures must be conveyed to an ECO (e.g., the VP-QA/EHS) and the laboratory's Quality Director within 24 hours of discovery.

Whether an inaccurate result was reported due to calculation or quantitation errors, data entry errors, improper practices, or failure to follow SOPs, the data must be evaluated to determine the possible effect.

The Laboratory Director, QA Manager, ECOs, VP of Operations and the Quality Directors have the authority and responsibility to halt work, withhold final reports, or suspend an analysis for due cause as well as authorize the resumption of work.

11.3) Evaluation of Significance and Actions Taken

For each nonconforming issue reported, an evaluation of its significance and the level of management involvement needed is made. This includes reviewing its impact on the final data, whether or not it is an isolated or systematic issue, and how it relates to any special client requirements.

The NDSC Document entitled Data Recalls (CW-Q-S-005) is the procedure to be followed when it is discovered that erroneous or biased data may have been reported to clients or regulatory agencies.

The NDSC Document entitled Internal Investigations (CW-L-S-002) is the procedure to be followed for investigation and correction of situations involved alleged incidents of misconduct or violation of the company's ethics policy.

Laboratory level decisions are documented and approved using the laboratory's standard nonconformance/corrective action reporting in lieu of the data recall determination form contained in NDSC Document No. CW-Q-S-005.

11.4) Prevention of Nonconforming Work

If it is determined that the nonconforming work could recur, further corrective actions must be made following the laboratory's corrective action system. Periodically as defined by the laboratory's preventive action schedule, the QA Department evaluates non-conformances to determine if any nonconforming work has been repeated multiple times. If so, the laboratory's corrective action process may be followed.

11.5) Method Suspension / Restriction (Stop Work Procedures)

In some cases, it may be necessary to suspend/restrict the use of a method or target analyte which constitutes significant risk and/or liability to the laboratory. Suspension/restriction procedures can be initiated by any of the persons noted in Section 11.2, Paragraph 4.
Prior to suspension/restriction, confidentiality will be respected, and the problem with the required corrective and preventive action will be stated in writing and presented to the Laboratory Director.

The Laboratory Director/BUMA shall arrange for the appropriate personnel to meet with the QA Manager as needed. This meeting shall be held to confirm that there is a problem, that suspension/restriction of the method is required and will be concluded with a discussion of the steps necessary to bring the method/target or test fully back on line. In some cases, that may not be necessary if all appropriate personnel have already agreed there is a problem and there is agreement on the steps needed to bring the method, target or test fully back on line. The QA Manager will also initiate a corrective action report as described in Section 12 if one has not already been started. A copy of any meeting notes and agreed upon steps should be e-mailed by the

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laboratory to their Business Unit President; VP-QA & EHS. This e-mail acts as notification of the incident.

After suspension/restriction, the lab will hold all reports to clients pending review. No faxing, mailing or distributing through electronic means may occur. The report must not be posted for viewing on the internet. It is the responsibility of the Laboratory Director to hold all reporting and to notify all relevant laboratory personnel regarding the suspension/restriction (e.g., Project Management, Log-in, etc.). Clients will NOT generally be notified at this time. Analysis may proceed in some instances depending on the non-conformance issue.

Within 72 hours, the QA Manager will determine if compliance is now met and reports can be released, OR determine the plan of action to bring work into compliance, and release work. A team, with all principals involved (e.g., Laboratory Director, Technical Manager, QA Manager) can devise a start-up plan to cover all steps from client notification through compliance and release of reports. Project Management and the Directors of Client Services and Sales and Marketing must be notified if clients must be notified or if the suspension/restriction affects the laboratory's ability to accept work. The QA Manager must approve start-up or elimination of any restrictions after all corrective action is complete.

12) CORRECTIVE ACTION

12.1) Overview

A major component of the laboratory's (QA) Program is the problem investigation and feedback mechanism designed to keep the laboratory staff informed on quality related issues and to provide insight to problem resolution. When nonconforming work or departures from policies and procedures in the quality system or technical operations are identified, the corrective action procedure provides a systematic approach to assess the issues, restore the laboratory's system integrity, and prevent reoccurrence. The laboratory employs two systems to manage non-conformances. Issues suspected of being systematic in nature and for which root cause analysis and a formal Corrective Action Report (CAR) are documented in the Incident Corrective Action Tracking (ICAT) database. Routine batch non-conformances, events that are understood to be isolated in nature, are documented in the LIMS non-conformance memo (NCM) system.

12.2) General

Problems within the quality system or within analytical operations may be discovered in a variety of ways, such as QC sample failures, internal or external audits, proficiency testing (PT) performance, client complaints, staff observation, etc.

The purpose of a corrective action system is to:

- Identify non-conformance events and assign responsibility for investigating.
- Resolve non-conformance events and assign responsibility for any required corrective action.
- Identify systematic problems before they become serious.
- Identify and track client complaints and provide resolution.

12.2.1) Non-Conformance Memo (NCM)

NCMs are used to document the following types of corrective actions:

- Deviations from an established procedure or SOP
- QC outside of limits
- Isolated reporting / calculation errors
- Client complaints
- Discrepancies in materials / goods received vs. manufacturer packing slips (Forms of documentation other than NCMs in LIMS are also acceptable)

12.2.2) Corrective Actions Documented In the iCAT Database

- Internal and external audit findings
- Failed or unacceptable PT results
- Identified poor process or method performance trends
- Systematic reporting / calculation errors
- Data recall investigations
- Questionable trends that are found in the review of NCMs.

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- Client complaints
- Excessive revised reports

The ICAT database is used to document background information, track the results of corrective action investigations and root cause analysis, and to provide reports of corrective action plans.

12.3) Closed Loop Corrective Action Process

Any employee in the company can initiate a corrective action. There are four main components to a closed-loop corrective action process once an issue has been identified: Cause Analysis, Selection and Implementation of Corrective Actions (both short and long term), Monitoring of the Corrective Actions, and Follow-up.

12.3.1) Cause Analysis

- Upon discovery of a non-conformance event, the event must be defined and documented. An entry into the ICAT system must be initiated, someone is assigned to investigate the issue and the event is investigated for cause. Table 12-1 provides some general guidelines on determining responsibility for assessment.
- The cause analysis step is the key to the process as a long term corrective action cannot be determined until the cause is determined.
- If the cause is not readily obvious, the Technical Manager, Laboratory Director/BUMA, or QA Manager (or QA designee) is consulted.

12.3.2) Selection and Implementation of Corrective Actions

- Where corrective action is needed, the laboratory shall identify potential corrective actions. The action(s) most likely to eliminate the problem and prevent recurrence are selected and implemented. Responsibility for implementation is assigned.
- Corrective actions shall be to a degree appropriate to the magnitude of the problem identified through the cause analysis.
- Whatever corrective action is determined to be appropriate, the laboratory shall document and implement the changes. The ICAT record is used for this documentation.

12.3.3) Root Cause Analysis

Root Cause Analysis is a class of problem solving (investigative) methods aimed at identifying the basic or causal factor(s) that underlie variation in performance or the occurrence of a significant failure. The root cause may be buried under seemingly innocuous events, many steps preceding the perceived failure. At first glance, the immediate response is typically directed at a symptom and not the cause. Typically, root cause analysis would be best with three or more incidents to triangulate a weakness. NDSC Document No. CA-Q-S-009, Root Cause Analysis, provides guidance on this procedure.

Systematically analyze and document the root causes of the more significant problems that are reported. Identify, track, and implement the corrective actions required to reduce the likelihood of recurrence of significant incidents. Trend the root cause data from these incidents to identify root causes that, when corrected, can lead to dramatic improvements in performance by eliminating entire classes of problems.

Identify the one event associated with problem and ask why this event occurred. Brainstorm the root causes of failures; for example, by asking why events occurred or conditions existed; and then why the cause occurred consecutive times until you get to the root cause. For each of these sub events or causes, ask why it occurred. Repeat the process for the other events associated with the incident.

Root cause analysis does not mean the investigation is over. Look at technique or other systems outside the normal indicators. Often creative thinking will find root causes that ordinarily would be missed and continue to plague the laboratory or operation.

12.3.4) Monitoring of the Corrective Actions

- The Technical Manager and QA Manager are responsible to ensure that the corrective action taken was effective.

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- Ineffective actions are documented and re-evaluated until acceptable resolution is achieved. Technical Managers are accountable to the Laboratory Director to ensure final acceptable resolution is achieved and documented appropriately.
- The QA Manager reviews monthly NCM and ICAT records for trends. Highlights are included in the QA monthly report (refer to Section 16). If a significant trend develops that adversely affects quality, an audit of the area is performed and corrective action implemented.
- Any out-of-control situations that are not addressed acceptably at the laboratory level may be reported to the NDSC Quality Director by the QA Manager, indicating the nature of the out-of-control situation and problems encountered in solving the situation.

12.3.5) Follow-up Audits

- Follow-up audits may be initiated by the QA Manager and shall be performed as soon as possible when the identification of a nonconformance casts doubt on the laboratory's compliance with its own policies and procedures, or on its compliance with state or federal requirements.
- These audits often follow the implementation of the corrective actions to verify effectiveness. An additional audit would only be necessary when a critical issue or risk to business is discovered.

(Also refer to Section 15.1.4, Special Audits.)

12.4) Technical Corrective Actions

In addition to providing acceptance criteria and specific protocols for technical corrective actions in the method SOPs, the laboratory has general procedures to be followed to determine when departures from the documented policies and procedures and quality control have occurred (refer to Section 11). The documentation of these procedures is through the use of an NCM or record in the ICAT system.

Table 12-1 includes examples of general technical corrective actions. For specific criteria and corrective actions, refer to the analytical methods or specific method SOPs. The laboratory may also maintain Work Instructions on these items that are available upon request.

Table 12-1 provides some general guidelines for identifying the individual(s) responsible for assessing each QC type and initiating corrective action. The table also provides general guidance on how a data set should be treated if associated QC measurements are unacceptable. Specific procedures are included in Method SOPs, Work Instructions, QA Manual Sections 19 and 20. All corrective actions are reviewed monthly, at a minimum, by the QA Manager and highlights are included in the QA monthly report.

To the extent possible, samples shall be reported only if all quality control measures are acceptable. If the deficiency does not impair the usability of the results, data will be reported with an appropriate data qualifier and/or the deficiency will be noted in the case narrative. Where sample results may be impaired, the PM is notified by an NCM and appropriate corrective action (e.g., reanalysis) is taken and documented.

12.5) Basic Corrections

When mistakes occur in records, each mistake shall be crossed-out, [not obliterated (e.g. no white-out)], and the correct value entered alongside. All such corrections shall be initialed (or signed) and dated by the person making the correction. In the case of records stored electronically, the original uncorrected file must be maintained intact and a second corrected file is created. This same process applies to adding additional information to a record. All additions made later than the initial must also be initialed (or signed) and dated. When corrections are due to reasons other than obvious transcription errors, the reason for the corrections (or additions) shall also be documented.

12.5) Table 12-1. Example – General Corrective Action Procedures

QC Activity (Individual Responsible for Initiation/Assessment)	Acceptance Criteria	Recommended Corrective Action

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QC Activity (Individual Responsible for Initiation/Assessment)	Acceptance Criteria	Recommended Corrective Action
Initial Instrument Blank (Analyst)	- Instrument response < MDL.	- Prepare another blank. - If same response, determine cause of contamination: reagents, environment, instrument equipment failure, etc..
Initial Calibration Standards (Analyst, Technical Manager(s))	- Correlation coefficient > 0.99 or standard concentration value. - % Recovery within acceptance range. - See details in Method SOP.	- Reanalyze standards. - If still unacceptable, remake standards and recalibrate instrument.
Independent Calibration Verification (Second Source) (Analyst, Technical Manager(s))	- % Recovery within control limits.	- Remake and reanalyze standard. - If still unacceptable, then remake calibration standards or use new primary standards and recalibrate instrument.
Continuing Calibration Standards (Analyst, Data Reviewer)	% Recovery within control limits.	- Reanalyze standard. - If still unacceptable, then recalibrate and rerun affected samples.
Matrix Spike / Matrix Spike Duplicate (MS/MSD) (Analyst, Data Reviewer)	- % Recovery within limits documented in **(state where limits are maintained)**.	- If the acceptance criteria for duplicates or matrix spikes are not met because of matrix interferences, the acceptance of the analytical batch is determined by the validity of the LCS. - If the LCS is within acceptable limits the batch is acceptable. - The results of the duplicates, matrix spikes and the LCS are reported with the data set. - For matrix spike or duplicate results outside criteria the data for that sample shall be reported with qualifiers.

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QC Activity (Individual Responsible for Initiation/Assessment)	Acceptance Criteria	Recommended Corrective Action
Laboratory Control Sample (LCS) (Analyst, Data Reviewer)	- % Recovery within limits specified in **(state where limits are maintained).**	- Batch must be re-prepared and re-analyzed. This includes any allowable marginal exceedance. When not using marginal exceedances, the following exceptions apply: 1) when the acceptance criteria for the positive control are exceeded high (i.e., high bias) and there are associated samples that are non-detects, then those non-detects may be reported with data qualifying codes; 2) when the acceptance criteria for the positive control are exceeded low (i.e., low bias), those sample results may be reported if they exceed a maximum regulatory limit/decision level with data qualifying codes. **Note:** If there is insufficient sample or the holding time cannot be met, contact client and report with flags.
Method Blank (MB) (Analyst, Data Reviewer)	< Reporting Limit 1	- Reanalyze blank. - If still positive, determine source of contamination. If necessary, reprocess (i.e. digest or extract) entire sample batch. Report blank results. - Qualify the result(s) if the concentration of a targeted analyte in the MB is at or above the reporting limit AND is > 1/10 of the amount measured in the sample.
Proficiency Testing (PT) Samples (QA Manager, Technical Manager(s))	- Criteria supplied by PT Supplier.	- Any failures or warnings must be investigated for cause. Failures may result in the need to repeat a PT sample to show the problem is corrected.
Internal / External Audits (QA Manager, Technical Manager(s), Laboratory Director)	- Defined in Quality System documentation such as SOPs, QAM, etc..	- Non-conformances must be investigated through CAR system and necessary corrections must be made.
Reporting / Calculation Errors (Depends on issue – possible individuals include: Analysts, Data Reviewers, Project Managers, Technical Managers, QA Manager, NDSC QA, Executive Management)	- NDSC Document No. CW-Q-S-005, Data Recall **or** local SOP No.	- Corrective action is determined by type of error. Follow the procedures in NDSC Document No. CW-L-S-002 **or** your lab's CA SOP.

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QC Activity (Individual Responsible for Initiation/Assessment)	Acceptance Criteria	Recommended Corrective Action
Client Complaints (Project Managers, Lab Director/Manager, Sales and Marketing)	-	- Corrective action is determined by the type of complaint. For example, a complaint regarding an incorrect address on a report will result in the report being corrected and then follow-up must be performed on the reasons the address was incorrect (e.g., database needs to be updated).
QA Monthly Report (Refer to Section 16 for an example) (QA Manager, Lab Director/Manager, Technical Manager(s))	- QAM, SOPs.	- Corrective action is determined by the type of issue. For example, CARs for the month are reviewed and possible trends are investigated.
Health and Safety Violation (Safety Officer, Lab Director/Manager, Technical Manager(s))	- Environmental Health and Safety (EHS) Manual.	- Non-conformance is investigated and corrected through CAR system.

Note:
1. Except as noted below for certain compounds, the method blank should be below the detection limit (1/2 detection level for DoD/DOE). Concentrations up to five times the reporting limit will be allowed for the ubiquitous laboratory and reagent contaminants: methylene chloride, toluene, acetone, 2-butanone and phthalates **provided** they appear in similar levels in the reagent blank and samples. This allowance presumes that the detection limit is significantly below any regulatory limit to which the data are to be compared and that blank subtraction will not occur. For benzene and ethylene dibromide (EDB) and other analytes for which regulatory limits are extremely close to the detection limit, the method blank must be below the method detection limit.

13) PREVENTIVE ACTION / IMPROVEMENT

13.1) Overview

The laboratory's preventive action programs improve or eliminate potential causes of nonconforming product and/or nonconformance to the quality system. This preventive action process is a proactive and continuous process of improvement activities that can be initiated through feedback from clients, employees, business providers, and affiliates. The QA Department has the overall responsibility to ensure that the preventive action process is in place, and that relevant information on actions is submitted for management review.

Dedicating resources to an effective preventive action system emphasizes the laboratory's commitment to its QA Program. It is beneficial to identify and address negative trends before they develop into complaints, problems and corrective actions. Additionally, the laboratory continually strives to improve customer service and client satisfaction through continuous improvements to laboratory systems.

Opportunities for improvement may be discovered through any of the following:

- review of the monthly QA Metrics Report,
- trending NCMs,
- review of control charts and QC results,
- trending proficiency testing (PT) results,
- performance of management system reviews,
- trending client complaints,
- review of processing operations, or

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- staff observations.

The monthly Management Systems Metrics Report shows performance indicators in all areas of the laboratory and quality system. These areas include revised reports, corrective actions, audit findings, internal auditing and data authenticity audits, client complaints, PT samples, holding time violations, SOPs, ethics training, etc. The metrics report is reviewed monthly by the laboratory management, NDSC QA Team and Local and Executive Management. These metrics are used in evaluating the management and quality system performance on an ongoing basis and provide a tool for identifying areas for improvement.

Items identified as continuous improvement opportunities to the management system may be issued as goals from the annual management systems review, recommendations from internal audits, white papers, Lessons Learned, Technical Services audit report, Technical Best Practices, or as Executive or management initiatives.

The laboratory's corrective action process is integral to implementation of preventive actions. A critical piece of the corrective action process is the implementation of actions to prevent further occurrence of a non-compliance event. Historical review of corrective action and non-conformances provides a valuable mechanism for identifying preventive action opportunities.

13.1.1 The following elements are part of a preventive action/process improvement system:

- Identification of an opportunity for preventive action or process improvement.
- Process for the preventive action or improvement.
- Define the measurements of the effectiveness of the process once undertaken.
- Execution of the preventive action or improvement.
- Evaluation of the plan using the defined measurements.
- Verification of the effectiveness of the preventive action or improvement.
- Close-Out by documenting any permanent changes to the Quality System as a result of the Preventive Action or Process Improvement. Documentation of Preventive Action/process Improvement is incorporated into the monthly QA reports, corrective action process and management review.

13.1.2 Any preventive actions/process improvement undertaken or attempted shall be taken into account during the annual Management Systems Review (Section 16). A highly detailed report is not required; however, a summary of successes and failures within the preventive action program is sufficient to provide management with a measurement for evaluation.

13.2) Management of Change

The Management of Change process is designed to manage significant events and changes that occur within the laboratory. Through these procedures, the potential risks inherent with a new event or change are identified and evaluated. The risks are minimized or eliminated through pre-planning and the development of preventive measures. The types of changes covered under this system include: Facility Changes, Major Accreditation Changes, Addition or Deletion to Division's Capabilities or Instrumentation, Key Personnel Changes, Laboratory Information Management System (LIMS) changes. This process is discussed in further detail in *EFGS-Q-QD-SOP2833*, Developing Effective Preventive Actions Through Risk Management.

14) CONTROL OF RECORDS

The laboratory maintains a records management system appropriate to its needs and that complies with applicable standards or regulations as required. The system produces unequivocal, accurate records that document all laboratory activities. The laboratory retains all original observations, calculations and derived data, calibration records and a copy of the analytical report for a minimum of five years after it has been issued. Exceptions for programs with longer retention requirements are discussed in Section 12.1.2.

14.1) Overview

The laboratory has established procedures for identification, collection, indexing, access, filing, storage, maintenance and disposal of quality and technical records. A record index is listed in Table 16-1. More detailed information on retention of specific records is provided in NDSC Document Nos. CW-L-P-001, Records Retention Policy and CW-L-WI-001, Records Retention/Storage Schedule. Quality records are maintained by the QA department in a database and files, which is backed up as

part of the regular laboratory backup. Records are of two types; either electronic or hard copy paper formats depending on whether the record is computer or hand generated (some records may be in both formats). Technical records are maintained by Technical Managers.

14.1) Table 16-1. Record Index

	Record Types [1]:	Retention Time:
Technical Records	- Raw Data - Logbooks[2] - Standards - Certificates - Analytical Records - MDLs/IDLs/DOCs - Lab Reports	5 Years from analytical report issue*
Official Documents	- Quality Assurance Manual (QAM) - Work Instructions - Policies - SOPs - Policy Memorandums - Manuals - Published Methods	Indefinitely
QA Records	- Certifications - Method and Software Validation / Verification Data	Indefinitely
QA Records	- Internal & External Audits/Responses - Corrective/Preventive Actions - Management Reviews - Data Investigation	5 Years from archival* **Data Investigation:** 5 years or the life of the affected raw data storage whichever is greater (beyond 5 years if ongoing project or pending investigation)
Project Records	- Sample Receipt & COC Documents - Contracts and Amendments - Correspondence - QAPP - SAP - Telephone Logbooks - Lab Reports	5 Years from analytical report issue*
Administrative Records	Financial and Business Operations	Refer to NDSC Doc. No. CW-L-WI-001
	EH&S Manual, Permits	Indefinitely
	Disposal Records	Indefinitely
	Employee Handbook	Indefinitely
	Personnel files, Employee Signature & Initials, Administrative Training Records (e.g., Ethics)	Refer to HR Manual
	Administrative Policies	Indefinitely
	Technical Training Records	7 years
	Legal Records	Indefinitely
	HR Records	Refer to NDSC Doc. No. CW-L-WI-001
	IT Records	Refer to NDSC Doc. No. CW-L-WI-001
	NDSC Governance Records	Refer to NDSC Doc. No. CW-L-WI-001
	Sales & Marketing	5 years
	Real Estate	Indefinitely

[1] Record Types encompass hardcopy and electronic records.

[2] Examples of Logbook types: Maintenance, Instrument Run, Preparation (standard and samples), Standard and Reagent Receipt, Archiving, Balance Calibration, Temperature (hardcopy or electronic records).

* Exceptions listed in Table 16-2.

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14.1.1 All records are stored and retained in such a way that they are secure and readily retrievable at the laboratory facility or an offsite location that provides a suitable environment to prevent damage or deterioration and to prevent loss at the laboratory or the Iron Mountain data storage facility. All records shall be protected against fire, theft, loss, environmental deterioration, and vermin. In the case of electronic records, electronic or magnetic sources, storage media are protected from deterioration caused by magnetic fields and/or electronic deterioration.

Access to the data is limited to laboratory and company employees and shall be documented with an access log. Records archived off-site are stored in a secure location where a record is maintained of any entry into the storage facility. Whether on-site or off-site storage is used, logs are maintained in each storage box to note removal and return of records. Retention of records are maintained on-site at the laboratory for at least 1 year after their generation and moved offsite for the remainder of the required storage time. Records are maintained for a minimum of five years unless otherwise specified by a client or regulatory requirement.

For raw data and project records, record retention shall be calculated from the date the project report is issued. For other records, such as NDSC Documents, QA, or Administrative Records, the retention time is calculated from the date the record is formally retired. Records related to the programs listed in Table 16-2 have lengthier retention requirements and are subject to the requirements in Section 14.2.

14.2) Programs with Longer Retention Requirements

Some regulatory programs have longer record retention requirements than the standard record retention time. These are detailed in Table 15-2 with their retention requirements. In these cases, the longer retention requirement is enacted. If special instructions exist such that client data cannot be destroyed prior to notification of the client, the container or box containing that data is marked as to who to contact for authorization prior to destroying the data.

14.2) Table 16-2. Example: Special Record Retention Requirements

Program	[1]Retention Requirement
DOE Hanford	5 years, Written approval must be received from DOE Hanford prior to disposal of analytical data
Commonwealth of MA – All environmental data 310 CMR 42.14	10 years
Housing and Urban Development (HUD) Environmental Lead Testing	10 years
Alaska	10 years
Louisiana – All	10 years
Navy Facilities Engineering Service Center (NFESC)	10 years
OSHA	30 years

[1]Note: Extended retention requirements must be noted with the archive documents or addressed in facility-specific records retention procedures.

14.2.1 The laboratory has procedures to protect and back-up records stored electronically and to prevent unauthorized access to or amendment of these records. All analytical data is maintained as hard copy or in a secure readable electronic format. For analytical reports that are maintained as copies in PDF format, refer to Section 17.15.1 for more information.

14.2.2 The record keeping system allows for historical reconstruction of all laboratory activities that produced the analytical data, as well as rapid recovery of historical data (Records stored off site should be accessible within 2 days of a request for such records). The history of the sample from when the laboratory took possession of the samples must be readily understood through the documentation. This shall include inter-laboratory transfers of samples and/or extracts.

- The records include the identity of personnel involved in sampling, sample receipt, preparation, or testing. All analytical work contains the initials (at least) of the personnel involved. The laboratory's copy of the COC is stored with the invoice and the work order sheet generated by LIMS. The chain of custody would indicate the name of the sampler. If any sampling notes are provided with a work order, they are kept with this package.

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- All information relating to the laboratory facilities' equipment, analytical test methods, and related laboratory activities, such as sample receipt, sample preparation, or data verification are documented.
- The record keeping system facilitates the retrieval of all working files and archived records for inspection and verification purposes. Instrument data is stored sequentially by instrument. A given day's analyses are maintained in the order of the analysis. Run logs are maintained for each instrument or method; a copy of each day's run log or instrument sequence is stored with the data to aid in re-constructing an analytical sequence. Where an analysis is performed without an instrument, bound logbooks or bench sheets are used to record and file data. Standard and reagent information is recorded in logbooks or entered into LIMS for each method as required.
- Changes to hardcopy records shall follow the procedures outlined in Section 10 and 17. Changes to electronic records in LIMS or instrument data are recorded in audit trails.
- The reason for a signature or initials on a document is clearly indicated in the records such as "sampled by," "prepared by," "reviewed by", or "analyzed by".
- All generated data except those that are generated by automated data collection systems, are recorded directly, promptly and legibly in permanent dark ink.
- Hard copy data may be scanned into PDF format for record storage as long as the scanning process can be verified in order to ensure that no data is lost and the data files and storage media must be tested to verify the laboratory's ability to retrieve the information prior to the destruction of the hard copy that was scanned.
- Also refer to Section 17.15.1 'Computer and Electronic Data Related Requirements'.

14.3) Technical and Analytical Records

14.3.1 The laboratory retains records of original observations, derived data and sufficient information to establish an audit trail, calibration records, staff records and a copy of each analytical report issued, for a minimum of five years unless otherwise specified by a client or regulatory requirement. The records for each analysis shall contain sufficient information to enable the analysis to be repeated under conditions as close as possible to the original. The records shall include the identity of laboratory personnel responsible for performance of each analysis and reviewing results.

14.3.2 Observations, data and calculations are recorded real-time and are identifiable to the specific task.

14.3.3 Changes to hardcopy records shall follow the procedures outlined in Section 10 and 17. Changes to electronic records in LIMS or instrument data are recorded in audit trails.

The essential information to be associated with analysis, such as strip charts, tabular printouts, computer data files, analytical notebooks, and run logs, include:

- Laboratory sample ID code;
- Date of analysis; time of analysis is also required if the holding time is seventy-two (72) hours or less, or when time critical steps are included in the analysis (e.g., drying times, incubations, etc.); instrumental analyses have the date and time of analysis recorded as part of their general operations. Where a time critical step exists in an analysis, location for such a time is included as part of the documentation in a specific logbook or on a benchsheet.
- Instrumentation identification and instrument operating conditions/parameters. Operating conditions/parameters are typically recorded in instrument maintenance logs where available.
- analysis type;
- all manual calculations and manual integrations;
- analyst's or operator's initials/signature;
- sample preparation including ID codes, volumes, weights, instrument printouts, meter readings, calculations, reagents;
- test results;
- standard and reagent origin, receipt, preparation, and use;
- calibration criteria, frequency and acceptance criteria;
- data and statistical calculations, review, confirmation, interpretation, assessment and reporting conventions;
- quality control protocols and assessment;
- electronic data security, software documentation and verification, software and hardware audits, backups, and records of any changes to automated data entries; and
- Method performance criteria including expected quality control requirements. These are indicated both in LIMS and on specific analytical report formats.

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14.3.4 All logbooks used during receipt, preparation, storage, analysis, and reporting of samples or monitoring of support equipment shall undergo a periodic, documented supervisory or peer review.

14.4) Laboratory Support Activities

In addition to documenting all the above-mentioned activities, the following are retained QA records and project records (previous discussions in this section relate where and how these data are stored):

- all original raw data, whether hard copy or electronic, for calibrations, samples and quality control measures, including analysts' work sheets and data output records (chromatograms, strip charts, and other instrument response readout records);
- a written description or reference to the specific test method used which includes a description of the specific computational steps used to translate parametric observations into a reportable analytical value;
- copies of final reports;
- archived SOPs;
- correspondence relating to laboratory activities for a specific project;
- all corrective action reports, audits and audit responses;
- proficiency test results and raw data; and
- results of data review, verification, and crosschecking procedures

14.4.1) Sample Handling Records

Records of all procedures to which a sample is subjected while in the possession of the laboratory are maintained. These include but are not limited to records pertaining to:

- sample preservation including appropriateness of sample container and compliance with holding time requirement;
- sample identification, receipt, acceptance or rejection and login;
- sample storage and tracking including shipping receipts, sample transmittal / COC forms; and
- procedures for the receipt and retention of samples, including all provisions necessary to protect the integrity of samples.

14.5) Administrative Records

The laboratory also maintains the administrative records in either electronic or hard copy form. Refer to Table 14-1.

14.6) Records Management, Storage and Disposal

All records (including those pertaining to test equipment), certificates and reports are safely stored, held secure and in confidence to the client. Certification related records are available upon request.

All information necessary for the historical reconstruction of data is maintained by the laboratory. Records that are stored only on electronic media must be supported by the hardware and software necessary for their retrieval.

Records that are stored or generated by computers or personal computers have hard copy, write-protected backup copies, or an electronic audit trail controlling access.

The laboratory has a record management system (a.k.a., document control) for control of laboratory notebooks, instrument logbooks, standards logbooks, and records for data reduction, validation, storage and reporting. Laboratory notebooks are issued on a per analysis basis, and are numbered sequentially. All data are recorded sequentially within a series of sequential notebooks. Bench sheets are filed sequentially. Standards are maintained in LIMS – no logbooks are used to record that data. Records are considered archived when noted as such in the records management system (a.k.a., document control.)

14.6.1) Transfer of Ownership

In the event that the laboratory transfers ownership or goes out of business, the laboratory shall ensure that the records are maintained or transferred according to client's instructions. Upon ownership transfer, record retention requirements shall be addressed in the ownership transfer agreement and the responsibility for maintaining archives is clearly established. In addition, in cases

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of bankruptcy, appropriate regulatory and state legal requirements concerning laboratory records must be followed. In the event of the closure of the laboratory, all records will revert to the control of NDSC. Should the entire company cease to exist, as much notice as possible will be given to clients and the accrediting bodies who have worked with the laboratory during the previous 5 years of such action.

14.6.2) Records Disposal

Records are removed from the archive and destroyed after 5 years unless otherwise specified by a client or regulatory requirement. On a project specific or program basis, clients may need to be notified prior to record destruction. Records are destroyed in a manner that ensures their confidentiality such as shredding, mutilation or incineration. (Refer to Tables 16-1 and 16-2).

Electronic copies of records must be destroyed by erasure or physically damaging off-line storage media so no records can be read.

If a third party records management company is hired to dispose of records, a "Certificate of Destruction" is required.

15) AUDITS

15.1) Internal Audits

Internal audits are performed to verify that laboratory operations comply with the requirements of the lab's quality system and with the external quality programs under which the laboratory operates. Audits are planned and organized by the QA staff. Personnel conducting the audits should be independent of the area being evaluated. Auditors will have sufficient authority, access to work areas, and organizational freedom necessary to observe all activities affecting quality and to report the assessments to laboratory management and**,** when requested**,** to Executive Management.

Audits are conducted and documented as described in the NDSC Document No. on performing Internal Auditing, SOP No. CW-Q-S-003 and Quality Assurance Internal Auditing Procedures, SOP No. *EFGS-Q-QD-SOP2989***.** The types and frequency of routine internal audits are described in Table 17-1. Special or ad hoc assessments may be conducted as needed under the direction of the QA staff.

15.1) Table 17-1. Types of Internal Audits and Frequency

Description	Performed by	Frequency
Quality Systems Audits	QA Department, QA approved designee, or NDSC QA	All areas of the laboratory annually
Method Audits QA Technical Audits	Joint responsibility: a) QA Manager or designee b) Technical Manager or Designee (Refer to NDSC CW-Q-S-003 or local SOP No. *EFGS-Q-QD-SOP2989*)	QA Technical Audits Frequency: 50% of methods annually
SOP Method Compliance	Joint responsibility: a) QA Manager or designee b) Technical Manager or Designee (Refer to NDSC CW-Q-S-003 or local SOP No. *EFGS-Q-QD-SOP2989*)	SOP Compliance Review Frequency: · Every 2 years · **100% of SOPs annually (DoD/DOE Methods)**
Special	QA Department or Designee	Surveillance or spot checks performed as needed, e.g., to confirm corrective actions from other audits.
Performance Testing	Analysts with QA oversight	Two successful per year for each TNI field of testing or as dictated by regulatory requirements

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15.1.1) Annual Quality Systems Audit

An annual quality systems audit is required to ensure compliance to analytical methods and SOPs, Eurofins Data Integrity and Ethics Policies (see Sec. 5.2), TNI quality systems, client and state requirements, and the effectiveness of the internal controls of the analytical process, including but not limited to data review, quality controls, preventive action and corrective action. The completeness of earlier corrective actions is assessed for effectiveness & sustainability. The audit is divided into sections for each operating or support area of the lab, and each section is comprehensive for a given area. The area audits may be performed on a rotating schedule throughout the year to ensure adequate coverage of all areas. This schedule may change as situations in the laboratory warrant.

15.1.2) QA Technical Audits

QA technical audits assess data authenticity and analyst integrity. These audits are based on client projects, associated sample delivery groups, and the methods performed. Reported results are compared to raw data to verify the authenticity of results. The validity of calibrations and QC results are compared to data qualifiers, footnotes, and case narratives. Documentation is assessed by examining run logs and records of manual integrations. Manual calculations are checked. Where possible, electronic audit miner programs (e.g., Chrom AuditMiner) are used to identify unusual manipulations of the data deserving closer scrutiny. QA technical audits will include all methods within a two-year period.

15.1.3) SOP Method Compliance

Compliance of all SOPs with the source methods and compliance of the operational groups with the SOPs will be assessed by the Technical Manager or qualified designee at least every two years. ***Annually for methods and administrative SOPs related to DoD/DOE programs.*** It is also recommended that the work of each newly hired analyst is assessed within 3 months of working independently, (e.g., completion of method IDOC). In addition, as analysts add methods to their capabilities, (new IDOC) reviews of the analyst work products will be performed within 3 months of completing the documented training.

15.1.4) Special Audits

Special audits are conducted on an as needed basis, generally as a follow up to specific issues such as client complaints, corrective actions, PT results, data audits, system audits, validation comments, regulatory audits or suspected ethical improprieties. Special audits are focused on a specific issue, and report format, distribution, and timeframes are designed to address the nature of the issue.

15.1.5) Performance Testing

The laboratory participates semi-annually in performance audits conducted through the analysis of PT samples provided by a third party. The laboratory generally participates in the following types of PT studies: Nonpotable Water and Soil

It is Eurofins policy that PT samples be treated as typical samples in the production process. Furthermore, where PT samples present special or unique problems, in the regular production process they may need to be treated differently, as would any special or unique request submitted by any client. The QA Manager must be consulted and in agreement with any decisions made to treat a PT sample differently due to some special circumstance.

Written investigations for unacceptable PT results are required. In some cases it may be necessary for blind QC samples to be submitted to the laboratory to show a return to control.

15.2) External Audits

External audits are performed when certifying agencies or clients conduct on-site inspections or submit performance testing samples for analysis. It is Eurofins policy to cooperate fully with regulatory authorities and clients. The laboratory makes every effort to provide the auditors with access to personnel, documentation, and assistance. Laboratory supervisors are responsible for providing corrective actions to the QA Manager who coordinates the response. Audit responses are due in the time allotted by the client or agency performing the audit.

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The laboratory cooperates with clients and their representatives to monitor the laboratory's performance in relation to work performed for the client. The client may only view data and systems related directly to the client's work. All efforts are made to keep other client information confidential.

15.2.1) Confidential Business Information (CBI) Considerations

During on-site audits, auditors may come into possession of information claimed as business confidential. A business confidentiality claim is defined as "a claim or allegation that business information is entitled to confidential treatment for reasons of business confidentiality or a request for a determination that such information is entitled to such treatment." When information is claimed as business confidential, the laboratory must place on (or attach to) the information at the time it is submitted to the auditor, a cover sheet, stamped or typed legend or other suitable form of notice, employing language such as "trade secret", "proprietary" or "company confidential". Confidential portions of documents otherwise non-confidential must be clearly identified. CBI may be purged of references to client identity by the responsible laboratory official at the time of removal from the laboratory. However, sample identifiers may not be obscured from the information. Additional information regarding CBI can be found in within the 2009 and 2016 TNI standards.

15.3) Audit Findings

Audit findings are documented using the corrective action process and database (see Section 12). The laboratory's corrective action responses may include action plans that could not be completed within a predefined timeframe. In these instances, a completion date must be set and agreed to by operations management and the QA Manager.

Developing and implementing corrective actions to findings is the responsibility of the Technical Manager where the finding originated. Findings that are not corrected by specified due dates are reported monthly to management in the QA monthly report.

If any audit finding casts doubt on the effectiveness of the operations or on the correctness or validity of the laboratory's test results, the laboratory shall take timely corrective action, and shall notify clients in writing if the investigations show that the laboratory results have been affected. Once corrective action is implemented, a follow-up audit is scheduled to ensure that the problem has been corrected.

Clients must be notified promptly in writing of any event such as the identification of defective measuring or test equipment that casts doubt on the validity of results given in any test report or amendment to a test report. The investigation must begin within 24 hours of discovery of the problem and all efforts are made to notify the client within two weeks after the completion of the investigation.

16) MANAGEMENT REVIEWS

16.1) Quality Assurance Report

The QA Department is responsible for preparing a comprehensive monthly metrics report to Management to keep them apprised of current quality issues. This report fosters communication, review, and refinement of the QA system to evaluate the suitability of policies and procedures to meet both regulatory and laboratory quality objectives.

The NDSC QA team compiles information from all of the Environment Testing laboratories monthly metrics reports for the Executive Management team. This report includes notable information and concerns regarding the laboratories QA program and a listing of new regulations that may potentially impact the laboratories.

16.2) Annual Management Review

The Laboratory Management team (Laboratory Director/BUMA, Technical Managers, QA Manager) conducts a review annually of its quality systems to ensure its continuing suitability and effectiveness in meeting client and regulatory requirements and to introduce any necessary changes or improvements. It will also provide a platform for defining goals, objectives and action items that feed into the laboratory planning system. NDSC personnel is be included in this meeting at the discretion of the Laboratory Director/BUMA. The LIMS review consists of examining any audits, complaints or concerns that have been raised through the year that are related to LIMS. The

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laboratory will summarize any critical findings that cannot be solved by the lab and report them to Corporate IT.

This management systems review (NDSC Document No. CW-Q-S-004 and Work Instruction No. CW-Q-WI-003) uses information generated during the preceding year to assess the "big picture" by ensuring that routine actions taken and reviewed on a monthly basis are not components of larger systematic concerns. The monthly review should keep the quality systems current and effective, therefore, the annual review is a formal senior management process to review specific existing documentation. Significant issues from the following documentation are compiled or summarized by the QA Manager prior to the review meeting:

- Matters arising from the previous annual review.
- Prior Monthly QA Reports issues.
- Laboratory QA Metrics.
- Review of report reissue requests.
- Review of client feedback and complaints.
- Issues arising from any prior management or staff meetings.
- Minutes from prior senior lab management meetings. Issues that may be raised from these meetings include:
  - Adequacy of staff, equipment and facility resources.
  - Adequacy of policies and procedures.
  - Future plans for resources and testing capability and capacity.
- The annual internal double blind PT program sample performance (if performed),
- Compliance to the Ethics Policy and Data Integrity Plan. Including any evidence/incidents of inappropriate actions or vulnerabilities related to data Integrity.
- For labs analyzing radioactive samples, also include the following:
  - Radiation health and safety
  - Radioactive hazardous waste management
  - Radioactive materials management
- Evaluation of overall risk, including risks to impartiality, confidentiality, reporting statements of conformity, and nonconforming work.
- A report is generated by the QA Manager and management. The report is distributed to the Laboratory Manager/BUMA, President of the Business Unit and Technical Managers. The report includes, but is not limited to:
- The date of the review and the names and titles of participants.
- A reference to the existing data quality related documents and topics that were reviewed.
- Quality system or operational changes or improvements that will be made as a result of the review [e.g., an implementation schedule including assigned responsibilities for the changes (Action Table)].

Changes to the quality systems requiring update to the laboratory QA Manual shall be included in the next revision of the QA Manual.

16.3) Potential Integrity Related Managerial Reviews

Potential integrity issues (data or business related) must be handled and reviewed in a confidential manner until such time as a follow-up evaluation, full investigation, or other appropriate actions have been completed and issues clarified. The NDSC Document No. CW-L-S-002, Internal Investigations shall be followed. All investigations that result in finding of inappropriate activity are documented and include any disciplinary actions involved, corrective actions taken, and all appropriate notifications of clients.

The Eurofins Environment Testing America Presidents, Business Unit Managers, Laboratory Directors, NDSC Team are informed of any current data integrity or data recall investigations via the monthly metrics report.

17) TEST METHODS AND METHOD VALIDATION

17.1) Overview

The laboratory uses methods that are appropriate to meet our clients' requirements and that are within the scope of the laboratory's capabilities. These include sampling, handling, transport, storage and preparation of samples, and, where appropriate, an estimation of the measurement of uncertainty as well as statistical techniques for analysis of environmental data.

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Instructions are available in the laboratory for the operation of equipment as well as for the handling and preparation of samples. All instructions, Standard Operating Procedures (SOPs), reference methods and manuals relevant to the working of the laboratory are readily available to all staff. Deviations from published methods are documented (with justification) in the laboratory's approved SOPs. SOPs are submitted to clients for review at their request. Significant deviations from published methods require client approval and regulatory approval where applicable.

17.2) Standard Operating Procedures (SOPs)

The laboratory maintains SOPs that accurately reflect all phases of the laboratory such as assessing data integrity, corrective actions, handling customer complaints as well as all analytical methods and sampling procedures. The method SOPs are derived from the most recently promulgated/approved, published methods and are specifically adapted to the laboratory facility. Modifications or clarifications to published methods are clearly noted in the SOPs. All SOPs are controlled in the laboratory.

- All SOPs contain a revision number, effective date, and appropriate approval signatures. Controlled copies are available to all staff.
- Procedures for writing an SOP are incorporated by reference to NDSC Document No. CW-Q-S-002, Writing a Standard Operating Procedure', and the laboratory's SOP *EFGS-Q-QD-SOP2804*, Creation and Control of Standard Operating Procedures
- SOPs are reviewed at a minimum of every 2 years (annually for DoD/DOE SOPs), and where necessary, revised to ensure continuing suitability and compliance with applicable requirements.

17.3) Laboratory Methods Manual

For each test method, the laboratory shall have available the published referenced method as well as the laboratory developed SOP.

Note: If more stringent standards or requirements are included in a mandated test method or regulation than those specified in this manual, the laboratory shall demonstrate that such requirements are met. If it is not clear which requirements are more stringent, the standard from the method or regulation is to be followed. Any exceptions or deviations from the referenced methods or regulations are noted in the specific analytical SOP.

The laboratory maintains an SOP Index for both technical and non-technical SOPs. Technical SOPs are maintained to describe a specific test method. Non-technical SOPs are maintained to describe functions and processes not related to a specific test method.

17.4) Selection of Methods

Since numerous methods and analytical techniques are available, continued communication between the client and laboratory is imperative to assure the correct methods are utilized. Once client methodology requirements are established, this and other pertinent information is summarized by the PM. These mechanisms ensure that the proper analytical methods are applied when the samples arrive for log-in. For non-routine analytical services (e.g., special matrices, non-routine compound lists), the method of choice is selected based on client needs and available technology. The methods selected should be capable of measuring the specific parameter of interest, in the concentration range of interest, and with the required precision and accuracy.

17.4.1) Sources of Methods

Routine analytical services are performed using standard EPA-approved methodology. In some cases, modification of standard approved methods may be necessary to provide accurate analyses of particularly complex matrices. When the use of specific methods for sample analysis is mandated through project or regulatory requirements, only those methods shall be used.

When clients do not specify the method to be used or methods are not required, the methods used will be clearly validated and documented in an SOP and available to clients and/or the end user of the data. Refer to Appendix 6 for a list of the currently accepted U.S. EPA analytical method references used by the laboratory.

The laboratory reviews updated versions to all the aforementioned references for adaptation based upon capabilities, instrumentation, etc., and implements them as appropriate. As such, the

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laboratory strives to perform only the latest versions of each approved method as regulations allow or require.

Other reference procedures for non-routine analyses may include methods established by specific states (e.g., Underground Storage Tank methods), ASTM or equipment manufacturers. Sample type, source, and the governing regulatory agency requiring the analysis will determine the method utilized.

The laboratory shall inform the client when a method proposed by the client may be inappropriate or out of date. After the client has been informed, and they wish to proceed contrary to the laboratory's recommendation, it will be documented.

17.4.1.1 Client Supplied Methods

Most of the client-supplied method requirements presented to us involve achieving specific quality control criteria, limits of quantitation (LOQ), and/or method detection limits (MDL) using standard EPA methods. These requirements are communicated to the appropriate technical groups prior to the project start up. Each technical group evaluates the scope of work and the requirements to ensure the criteria can be met using the standard EPA method. The data is monitored to ensure the criteria are met throughout the project. The PM notifies the client if there is a more appropriate method available or if the client's criteria cannot be achieved on a certain sample matrix (i.e., due to matrix or dilutions).

Occasionally, we are asked to transfer a non-standardized method from a client into our lab or to develop a new method, when one is not available. In the case of a method transfer, we set up the client's method and perform some initial evaluation. After the initial evaluation, we may make recommendations on how to improve method performance. If the method appears to be adequate, we determine linearity, specificity, precision, accuracy, MDL, and LOQ by performing calibrations, analyzing method blanks, and carrying out method detection limit and IDOC studies.

In the case of method development, we work with the client and/or data user to determine the level of validation required ensuring that the method meets its intended purpose. In addition to the elements above, we also determine standard and sample stability and robustness depending on the scope of the project. Typically, a standard operating procedure is written and submitted to the client with the results of the validation. These steps are completed prior to analysis of field samples. Data related to the setup of the method are archived.

17.4.1.2 Procedural Deviations

Analysts are required to follow a documented method for all tests performed; and any deviations from analytical methods must be documented, approved, and justified in an appropriate and consistent manner. We classify method deviations as either being a planned deviation or an unplanned deviation. In general, the following information is captured to document both types of situations:

- Description of the situation
- Reason or justification for the deviation
- Impact the deviation had on the testing
- Signature/date of analyst performing the test
- Signature/date of QA and Laboratory management approving the deviation
- Signature/date of client approval, if necessary

Deviations to written procedures are documented in raw data records, ICAT or through the ICAR (Investigation and Corrective Action Report) system. Both types of documentation require management and QA review and approval.

17.4.2) Demonstration of Capability

performance of the method in real world samples, but in an applicable and available clean matrix sample. If the method is for the testing of analytes that are not conducive to spiking, demonstration of capability may be performed on quality control samples.

A demonstration of capability, DOC (SOP# *EFGS-Q-QD-SOP2814*, Personnel Training and Demonstration of Capability Procedures) is performed whenever there is a change in instrument type (e.g., new instrumentation), matrix, method or personnel (e.g., analyst has not performed the test within the last 12 months).

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Note: The laboratory shall have a DOC for all analytes included in the methods that the laboratory performs, and proficiency DOCs for each analyst shall include all analytes that the laboratory routinely performs. Addition of non-routine analytes does not require new DOCs for all analysts if those analysts are already qualified for routine analytes tested using identical chemistry and instrument conditions.

The initial demonstration of capability must be thoroughly documented and approved by the Technical Manager and QA Manager prior to independently analyzing client samples. All associated documentation must be retained in accordance with the laboratory's archiving procedures.

The laboratory must have an approved SOP, demonstrate satisfactory performance, and conduct an MDL study (when applicable). There may be other requirements as stated within the published method or regulations (e.g., retention time window study).

Note: In some instances, a situation may arise where a client requests that an unusual analyte be reported using a method where this analyte is not normally reported. If the analyte is being reported for regulatory purposes, the method must meet all procedures outlined within this QA Manual (SOP, MDL, and Demonstration of Capability). If the client states that the information is not for regulatory purposes, the result may be reported as long as the following criteria are met:

- The instrument is calibrated for the analyte to be reported using the criteria for the method and ICV/CCV criteria are met (unless an ICV/CCV is not required by the method or criteria are per project DQOs).
- The laboratory's nominal or default reporting limit (RL) is equal to the quantitation limit (QL), must be at or above the lowest non-zero standard in the calibration curve and must be reliably determined. Project RLs are client specified reporting levels which may be higher than the QL. Results reported below the QL must be qualified as estimated values. Also see Section 17.6.1.3, Relationship of Limit of Detection (LOD) to Quantitation Limit (QL).
- The client request is documented and the lab informs the client of its procedure for working with unusual compounds. The final report must be footnoted: *Reporting Limit based on the low standard of the calibration curve.*

17.4.3) Initial Demonstration of Capability (IDOC) Procedures

17.4.3.1 The spiking standard used must be prepared independently from those used in instrument calibration.

17.4.3.2 The analyte(s) shall be diluted in a volume of clean matrix sufficient to prepare four aliquots at the concentration specified by a method or the laboratory SOP.

17.4.3.3 At least four aliquots shall be prepared (including any applicable clean-up procedures) and analyzed according to the test method (either concurrently or over a period of days).

17.4.3.4 Using all of the results, calculate the mean recovery in the appropriate reporting units and the standard deviations for each parameter of interest.

17.4.3.5 When it is not possible to determine the mean and standard deviations, such as for presence, absence and logarithmic values, the laboratory will assess performance against criteria described in the Method SOP.

17.4.3.6 Compare the information obtained above to the corresponding acceptance criteria for precision and accuracy in the test method (if applicable) or in laboratory generated acceptance criteria (LCS or interim criteria) if there is no mandatory criteria established. If any one of the parameters do not meet the acceptance criteria, the performance is unacceptable for that parameter.

17.4.3.7 When one or more of the tested parameters fail at least one of the acceptance criteria, the analyst must proceed according to either option listed below:

- Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with 17.4.3.3 above.
- Beginning with 17.4.3.3 above, repeat the test for all parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this

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occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with 17.4.3.1 above.

Note: Results of successive LCS analyses can be used to fulfill the DOC requirement.

17.5) Laboratory Developed Methods and Non-Standard Methods

Any new method developed by the laboratory must be fully defined in an SOP and validated by qualified personnel with adequate resources to perform the method. Method specifications and the relation to client requirements must be clearly conveyed to the client if the method is a non-standard method (not a published or routinely accepted method). The client must also be in agreement to the use of the non-standard method.

17.6) Validation of Methods

Validation is the confirmation by examination and the provision of objective evidence that the particular requirements for a specific intended use are fulfilled.

All non-standard methods, laboratory designed/developed methods, standard methods used outside of their scope, and major modifications to published methods must be validated to confirm they are fit for their intended use. The validation will be as extensive as necessary to meet the needs of the given application. The results are documented with the validation procedure used and contain a statement as to the fitness for use.

17.6.1) Method Validation and Verification Activities for All New Methods

While method validation can take various courses, the following activities can be required as part of method validation. Method validation records are designated QC records and are archived accordingly.

When changes are made to any validated methods, the influence of such changes shall be documented and, if appropriate, a new validation shall be performed.

17.6.1.1 Determination of Method Selectivity – Method selectivity is the demonstrated ability to discriminate the analyte(s) of interest from other compounds in the specific matrix or matrices from other analytes or interference. In some cases to achieve the required selectivity for an analyte, a confirmation analysis is required as part of the method.

17.6.1.2 Determination of Method Sensitivity – Sensitivity can be both estimated and demonstrated. Whether a study is required to estimate sensitivity depends on the level of method development required when applying a particular measurement system to a specific set of samples. Detection limit studies are conducted as described in Section 19.7. Where other protocols for estimations and/or demonstrations of sensitivity are required by regulation or client agreement, these shall be followed.

17.6.1.3 Relationship of Limit of Detection (LOD) to the Limit of Quantitation (LOQ) – An important characteristic of expression of sensitivity is the distinction between the LOD and the LOQ. The LOD is the minimum level at which the presence of an analyte can be reliably concluded. The LOQ is the minimum concentration of analyte that can be quantitatively determined with acceptable precision and bias, equivalent to the laboratory's routine reporting limit (RL). For most instrumental measurement systems, there is a region where semi-quantitative data is generated around the LOD (both above and below the estimated MDL or LOD) and below the LOQ. In this region, detection of an analyte may be confirmed but quantification of the analyte is unreliable within the accuracy and precision guidelines of the measurement system. When an analyte is detected below the LOQ, and the presence of the analyte is confirmed by meeting the qualitative identification criteria for the analyte, the analyte can be reliably reported, but the amount of the analyte can only be estimated. If data is to be reported in this region, it must be done so with a qualification that denotes the semi-quantitative nature of the result.

17.6.1.4 Determination of Interferences – A determination that the method is free from interferences in a blank matrix is performed.

17.6.1.5 Determination of Range – Where appropriate to the method, the quantitation range is determined by comparison of the response of an analyte in a curve to established or targeted criteria. Generally the upper quantitation limit is defined by highest acceptable calibration

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concentration. The lower quantitation limit or QL cannot be lower than the lowest non-zero calibration level, and can be constrained by required levels of bias and precision.

17.6.1.6 Determination of Accuracy and Precision – Accuracy and precision studies are generally performed using replicate analyses, with a resulting percent recovery and measure of reproducibility (standard deviation, relative standard deviation) calculated and measured against a set of target criteria.

17.6.1.7 Documentation of Method – The method is formally documented in an SOP. If the method is a minor modification of a standard laboratory method that is already documented in an SOP, an SOP Attachment describing the specific differences in the new method is acceptable in place of a separate SOP.

17.6.1.8 Continued Demonstration of Method Performance – Continued demonstration of method performance is addressed in the SOP. Continued demonstration of method performance is generally accomplished by batch specific QC samples such as LCS, method blanks or PT samples.

17.7) Method Detection Limit (MDL) / Limits of Detection (LOD)

The MDL is the minimum measured quantity of a substance that can be reported with 99% confidence that the concentration is distinguishable from method blank results, consistent with 40CFR Part 136 Appendix B, August, 2017. The MDL is equivalent to the TNI LOD or DL, and is also equivalent to the DoD/DOE Quality Systems Manual (QSM) DL. The working or final MDL is the higher of the MDL value determined from spikes (MDLs) and the MDL value determined from blanks (MDLb). An initial MDL study shall be performed during the method validation process and when the method is altered in a way that can reasonably be expected to change its sensitivity. On-going data are collected during each quarter in which samples are being analyzed. At least once every 13 months the MDLs and MDLb are re-calculated and re-evaluated using data collected during the preceding period. Details of the laboratory's procedure for conducting MDL studies are given in NDSC Document No. CA-Q-S-006.

17.8) Verification of Detection Limits

If it is found during the re-evaluation of detection limit results that more than 5% of the spiked samples do not return positive numeric results that meet all method qualitative identification criteria, then then spiking level shall be increased and the initial MDL study pre-performed at the new spiking concentration. For DoD/DOE labs, additional guidance provided in NDSC Document No. CA-Q-S-006 - Attachment 2.

17.9) Instrument Detection Limits (IDL)

The IDL is sometimes used to assess the reasonableness of the MDL or in some cases required by the analytical method or program requirements. IDLs are most commonly used in metals analyses but may be useful in demonstration of instrument performance in other areas.

IDLs are calculated to determine an instrument's sensitivity independent of any preparation method. IDLs are calculated either using 7 replicate spike analyses, like MDL but without sample preparation, or by the analysis of 10 instrument blanks and calculating 3 x the absolute value of the standard deviation.

17.10) Limit of Quantitation

The LOQ shall be at a concentration equivalent to the lowest calibration standard concentration, with the exception of methods using a single-point calibration, and shall be greater than the MDL. The LOQ is verified by preparing and analyzing spikes at concentrations 1-2X the selected LOQ, employing the complete analytical process. For DoD/DOE labs, additional requirements provided in NDSC Document No. CA-Q-S-006.

When the laboratory establishes a quantitation limit, it must be initially verified by the analysis of a low level standard or QC sample at 1-2 times the reporting limit or by a DL check samples at or below the LOQ. The LOQ is verified annually thereafter. The annual requirement is waived for methods that have an annually verified MDL. The laboratory will comply with any regulatory requirements.

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17.11) Retention Time Windows
Most organic analyses and some inorganic analyses use chromatography techniques for qualitative and quantitative determinations. For every chromatography analysis or as specified in the reference method, each analyte will have a specific time of elution from the column to the detector. This is known as the analyte's retention time. The variance in the expected time of elution is defined as the retention time window. As the key to analyte identification in chromatography, retention time windows must be established on every column for every analyte used for that method. These records are kept on-file and available for review. Complete details are available in the laboratory SOPs.

17.12) Evaluation of Selectivity
The laboratory evaluates selectivity by following the checks within the applicable analytical methods, which include mass spectral tuning, second column confirmation, ICP interelement interference checks, chromatography retention time windows, sample blanks, spectrochemical, atomic absorption or fluorescence profiles, co-precipitation evaluations and specific electrode response factors.

17.13) Estimation of Uncertainty of Measurement
17.13.1 Uncertainty is "a parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand" (as defined by the International Vocabulary of Basic and General Terms in Metrology, ISO Geneva, 1993, ISBN 92-67-10175-1). Knowledge of the uncertainty of a measurement provides additional confidence in a result's validity. Its value accounts for all the factors which could possibly affect the result, such as adequacy of analyte definition, sampling, matrix effects and interferences, climatic conditions, variances in weights, volumes, and standards, analytical procedure, and random variation. Some national accreditation organizations require the use of an "expanded uncertainty" defined as the range within which the value of the measurand is believed to lie within at least a 95% confidence level with the coverage factor k=2.

17.13.2 Uncertainty is not error. Error is a single value (i.e., the difference between the true result and the measured result). On environmental samples, the true result is never known. The measurement is the sum of the unknown true value and the unknown error. Unknown error is a combination of systematic error, or bias, and random error. Bias varies predictably, constantly, and independently from the number of measurements. Random error is unpredictable, assumed to be Gaussian in distribution, and reducible by increasing the number of measurements.

17.13.3 The minimum uncertainty associated with results generated by the laboratory can be determined by using the Laboratory Control Sample (LCS) accuracy range for a given analyte. The LCS limits are used to assess the performance of the measurement system since they take into consideration all of the laboratory variables associated with a given test over time (except for variability associated with the sampling and the variability due to matrix effects). The percent recovery of the LCS is compared either to the method-required LCS accuracy limits or to the statistical, historical, in-house LCS accuracy limits.

17.13.4 To calculate the uncertainty for the specific result reported, multiply the result by the decimal of the lower end of the LCS range percent value for the lower end of the uncertainty range, and multiply the result by the decimal of the upper end of the LCS range percent value for the upper end of the uncertainty range. These calculated values represent uncertainties at approximately the 99% confidence level with a coverage factor of k = 3. As an example, for a reported result of 1.0 mg/L with an LCS recovery range of 50 to 150%, the estimated uncertainty in the result would be 1.0 +/- 0.5 mg/L.

17.13.5 In the case where a well-recognized test method specifies limits to the values of major sources of uncertainty of measurement (e.g., 524.2, 525, etc.) and specifies the form of presentation of calculated results, no further discussion of uncertainty is required.

17.14) Sample Reanalysis Guidelines
Because there is a certain level of uncertainty with any analytical measurement, a sample re-preparation (where appropriate) and subsequent analysis (hereafter referred to as 'reanalysis') may result in either a higher or lower value from an initial sample analysis. There are also variables that may be present (e.g., sample homogeneity, analyte precipitation over time, etc.) that may affect the results of a reanalysis. Based on the above comments, the laboratory will reanalyze samples at a

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client's request with the following caveats. **Client specific Contractual Terms & Conditions for reanalysis protocols may supersede the following items.**

Homogenous samples: If a reanalysis agrees with the original result to within the RPD limits for MS/MSD or Duplicate analyses, or within + 1 reporting limit for samples < 5x the reporting limit, the original analysis will be reported. At the client's request, both results may be reported on the same report but not on two separate reports.

- If the reanalysis does not agree (as defined above) with the original result, then the laboratory will investigate the discrepancy and reanalyze the sample a third time for confirmation if sufficient sample is available.
- Any potential charges related to reanalysis are discussed in the contract terms and conditions or discussed at the time of the request. The client will typically be charged for reanalysis unless it is determined that the lab was in error.
- Due to the potential for increased variability, reanalysis may not be applicable to Non-homogenous, Encore, and Sodium Bisulfate preserved samples. See the Area Supervisor or Laboratory Director if unsure.

17.15) Control of Data

The laboratory has policies and procedures in place to ensure the authenticity, integrity, and accuracy of the analytical data generated by the laboratory.

17.15.1) Computer and Electronic Data Related Requirements

The three basic objectives of our computer security procedures and policies are shown below.

The laboratory is currently using TALS LIMS systems, which has been highly customized to meet the needs of the laboratory.

17.15.1.1 Maintain the Database Integrity – Assurance that data is reliable and accurate through data verification (review) procedures, password-protecting access, anti-virus protection, data change requirements, as well as an internal LIMS permissions procedure.

- LIMS Database Integrity is achieved through data input validation, internal user controls, documentation of system failures and corrective actions taken, and data change requirements.
- Spreadsheets and other software developed in-house must be verified with documentation through hand calculations prior to use. Cells containing calculations must be lock-protected and controlled.
- Instrument hardware and software adjustments are safeguarded through maintenance logs, audit trails and controlled access.

17.15.1.2 Ensure Information Availability – Protection against loss of information or service is ensured through scheduled back-ups, stable file server network architecture, secure storage of media, line filter, Uninterruptible Power Supply (UPS), and maintaining older versions of software as revisions are implemented.

17.15.1.3 Maintain Confidentiality – Ensure data confidentiality through physical access controls such as password protection or website access approval when electronically transmitting data.

17.15.2) Data Reduction

The complexity of the data reduction depends on the analytical method and the number of discrete operations involved (e.g., extractions, dilutions, instrument readings and concentrations). The analyst calculates the final results from the raw data or uses appropriate computer programs to assist in the calculation of final reportable values.

For manual data entry, e.g., Wet Chemistry, the data is reduced by the analyst and then verified by the Department Manager or alternate analyst prior to updating the data in LIMS. The spreadsheets, or any other type of applicable documents, are signed by both the analyst and alternate reviewer to confirm the accuracy of the manual entry(s).

Manual integration of peaks will be documented and reviewed and the raw data will be flagged using NDSC Document No. CA-Q-S-002, Acceptable Manual Integration Practices.

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Analytical results are reduced to appropriate concentration units specified by the analytical method, taking into account factors such as dilution, sample weight or volume, etc. Blank correction will be applied only when required by the method or per manufacturer's indication; otherwise, it should not be performed. Calculations are independently verified by appropriate laboratory staff. Calculations and data reduction steps for various methods are summarized in the respective analytical SOPs or program requirements.

17.15.2.1 All raw data must be retained in the worklist folder, computer file (if appropriate), and/or runlog. All criteria pertinent to the method must be recorded. The documentation is recorded at the time observations or calculations are made and must be signed or initialed/dated (month/day/year). It must be easily identifiable who performed which tasks if multiple people were involved.

17.15.2.2 In general, concentration results are reported in milligrams per liter (mg/l) or micrograms per liter (µg/l) for liquids and milligrams per kilogram (mg/kg) or micrograms per kilogram (µg/kg) for solids. For values greater than 10,000 mg/l, results can be reported in percent, i.e., 10,000 mg/l = 1%. Units are defined in each lab SOP.

17.15.2.3 In reporting, the analyst or the instrument output records the raw data result using values of known certainty plus one uncertain digit. If final calculations are performed external to LIMS, the results should be entered in LIMS with at least three significant figures. In general, results are reported to 2 significant figures on the final report.

17.15.2.4 For those methods that do not have an instrument printout or an instrumental output compatible with the LIMS, the raw results and dilution factors are entered directly into LIMS by the analyst, and the software calculates the final result for the analytical report. LIMS has a formatter for significant figure criterion for each analyte.

17.15.2.5 The laboratory strives to import data directly from instruments or calculation spreadsheets to ensure that the reported data are free from transcription and calculation errors. For those analyses with an instrumental output compatible with the LIMS, the raw results and dilution factors are transferred into LIMS, electronically after reviewing the quantitation report, and removing unrequested or poor spectrally-matched compounds. The analyst prints a copy of what has been entered to check for errors. This printout and the instrument's printout of calibrations, concentrations, retention times, chromatograms, and mass spectra, if applicable, are retained with the data file. The data file is stored in a monthly folder on the instrument computer; periodically, this file is transferred to the server and, eventually, to a tape file.

17.15.3) Logbook / Worksheet Use Guidelines

Logbooks and worksheets are filled out 'real time' and have enough information on them to trace the events of the applicable analysis/task. (e.g. calibrations, standards, analyst, sample ID, date, time on short holding time tests, temperatures when applicable, calculations are traceable, etc.)

- Corrections are made following the procedures outlined in Section 12.
- Logbooks are controlled by the QA department. A record is maintained of all logbooks in the lab.
- Unused portions of pages must be "Z"'d out, signed and dated.
- Worksheets are created with the approval of the Technical Manager/QA Manager at the facility. The QA Manager controls all worksheets following the procedures in Section 5.

17.15.4) Review / Verification Procedures

Review procedures are outlined in the SOP Data Review and Validation, *EFGS-P-DR-SOP2801* to ensure that reported data are free from calculation and transcription errors, that QC parameters have been reviewed and evaluated before data is reported. The general review concepts are discussed below, more specific information can be found in the SOP.

17.15.4.1 Log-In Review - The data review process starts at the sample receipt stage. Sample control personnel review chain-of-custody forms and project instructions from the project management group. This is the basis of the sample information and analytical instructions entered into the LIMS. The log-in instructions are reviewed by the personnel entering the information, and a second level review is conducted by the project management staff.

17.15.4.2 First Level Data Review - The next level of data review occurs with the analysts. As data are generated, analysts review their work to ensure that the results meet project and SOP

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requirements. First level reviews include inspection of all raw data (e.g., instrument output for continuous analyzers, chromatograms, spectra, and manual integrations), evaluation of calibration/calibration verification data in the day's analytical run, evaluation of QC data, and reliability of sample results. The analyst transfers data into LIMS, data qualifiers are added as needed. All first level reviews are documented.

17.15.4.3 Second Level Data Review – All analytical data are subject to review by a second qualified analyst or supervisor. Second level reviews include inspection of all raw data (e.g., instrument output, chromatograms, and spectra) including 100% of data associated with any changes made by the primary analyst, such as manual integrations or reassignment of peaks to different analytes, or elimination of false negative analytes. The second review also includes evaluation of initial calibration/calibration verification data in the day's analytical run, evaluation of QC data, reliability of sample results, qualifiers and NCM narratives. Manual calculations are checked in second level review. All second level reviews are documented.

Issues that deem further review include the following:

- QC data are outside the specified control limits for accuracy and precision
- Reviewed sample data does not match with reported results
- Unusual detection limit changes are observed
- Samples having unusually high results
- Samples exceeding a known regulatory limit
- Raw data indicating some type of contamination or poor technique
- Inconsistent peak integration
- Transcription errors
- Results outside of calibration range

17.15.4.4 Unacceptable analytical results may require reanalysis of the samples. Any problems are brought to the attention of the Laboratory Director, Project Manager, Quality Director/Manager, Technical Manager, or Supervisor for further investigation. Corrective action is initiated whenever necessary.

17.15.4.5 The results are then entered or directly transferred into the computer database and a (pdf) is printed for the client.

17.15.4.6 As a final review prior to the release of the report, the Project Manager reviews the results for appropriateness and completeness. This review and approval ensures that client requirements have been met and that the final report has been properly completed. The process includes, but is not limited to, verifying that the COC is followed, cover letters / narratives are present, flags are appropriate, and project specific requirements are met. The Project Manager may also evaluate the validity of results for different test methods given expected chemical relationships.

17.15.4.7 Any project that requires a data package is subject to a tertiary data review for transcription errors and acceptable quality control requirements. The Project Manager then signs the final report. The accounting personnel also check the report for any clerical or invoicing errors. When complete, the report is sent out to the client.

17.15.4.8 A brief overview of sample flow and information through the laboratory, as well as data review and validation, is presented in Figure 17-1.

17.15.5) Manual Integrations

Computerized data systems provide the analyst with the ability to re-integrate raw instrument data in order to optimize the interpretation of the data. Though manual integration of data is an invaluable tool for resolving variations in instrument performance and some sample matrix problems, when used improperly, this technique would make unacceptable data appear to meet quality control acceptance limits. Improper re-integrations lead to legally indefensible data, a poor reputation, or possible laboratory decertification. Because guidelines for re-integration of data are not provided in the methods and most methods were written prior to widespread implementation of computerized data systems, the laboratory trains all analytical staff on proper manual integration techniques using NDSC Document No. CA-Q-S-002, Acceptable Manual Integration Practices.

17.15.5.1 The analyst must adjust baseline or the area of a peak in some situations, for example when two compounds are not adequately resolved or when a peak shoulder needs to be separated from the peak of interest. The analyst must use professional judgment to determine when manual

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integrating is required. Analysts are encouraged to ask for assistance from a senior analyst or manager when in doubt.

17.15.5.2 Analysts shall not increase or decrease peak areas for the sole purpose of achieving acceptable QC recoveries that would have otherwise been unacceptable. The intentional recording or reporting of incorrect information (or the intentional omission of correct information) is against company principles and policy and is grounds for immediate termination.

17.15.5.3 Client samples, performance evaluation samples, and quality control samples are all treated equally when determining whether or not a peak area or baseline should be manually adjusted.

17.15.5.4 All manual integrations receive a second level review. Manual integrations must be indicated on expanded scale "before" and "after" chromatograms such that the integration performed can be easily evaluated during data review. Expanded scale "before" chromatograms are also required for all manual integrations on QC parameters (calibrations, calibration verifications, laboratory control samples, internal standards, surrogates, etc.) unless the laboratory has another documented NDSC approved procedure in place that can demonstrate an active process for detection and deterrence of improper integration practices.

17.15.5) Figure 17-1. Example – Work Flow

Action	Personnel Involved
Bottle orders generated upon request - Bottles packed and shipped to the client under CoC	- Client Service Personnel / PM - Bottle Preparation Personnel
Samples received at laboratory - Unpacked and reconciled against client paperwork or CoC - Samples acceptance documented against completed (CoC)[1]	Sample Login Personnel
Samples are entered into LIMS - Work Order # assigned - Methods/Analytes linked from project - Sample labels generated - LIMS backlogs updated immediately	Sample Login Personnel
Sample Storage - Short TATs and hold-time samples are delivered directly to the laboratory for analysis - Samples stored in assigned locations (refrigerated walk-in coolers, freezers; etc.)	Sample Login Personnel
Sample Receipt Acknowledgement sent to client (when requested)	Project Management Assistants / Project Management
Sample Acquisition/Testing - Analysts collect samples from assigned storage. - Legal CoC samples are signed in-and-out of storage - Remaining sample returned to storage.	Analysts / Login Personnel
Preparation and analysis is performed according to selected analytical method and applicable Project notes - Raw data recorded/reviewed[2] - Data imported to LIMS	Analysts
LIMS performs calculations: - Data reviewed by primary/secondary analyst - Data approved as final	Data Process (LIMS / Analyst)
Generation/review/release of reports (automated through LIMS) - Electronic copy saved in LIMS	Project Management Assistants / Project Management
Electronic Data Deliverables (EDDs) generated (as applicable)	Project Management Assistants / Project Management
Hard copy and electronic batch raw data is archived according to data archiving procedures.	Analysts / IT

[1]Refer to Sec. 21.3.

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[2]Analyses requiring the analyst's interpretation may involve manual data reduction before entry into LIMS.

18) EQUIPMENT and CALIBRATIONS

18.1) Overview

The laboratory purchases the most technically advanced analytical instrumentation for sample analyses. Instrumentation is purchased on the basis of accuracy, dependability, efficiency and sensitivity. Each laboratory is furnished with all items of sampling, preparation, analytical testing and measurement equipment necessary to correctly perform the tests for which the laboratory has capabilities. Each piece of equipment is capable of achieving the required accuracy and complies with specifications relevant to the method being performed. Before being placed into use, the equipment (including sampling equipment) is calibrated and checked to establish that it meets its intended specification. The calibration routines for analytical instruments establish the range of quantitation. Calibration procedures are specified in laboratory SOPs. A list of available laboratory instrumentation is presented in Table 18-1.

Equipment is only operated by authorized and trained personnel. Manufacturer's instructions for equipment use are readily accessible to all appropriate laboratory personnel.

18.2) Preventive Maintenance

The laboratory follows a well-defined maintenance program to ensure proper equipment operation and to prevent the failure of laboratory equipment or instrumentation during use. This program of preventive maintenance helps to avoid delays due to instrument failure.

Routine preventive maintenance procedures and frequency, such as cleaning and replacements, should be performed according to the procedures outlined in the manufacturer's manual. Qualified personnel must also perform maintenance when there is evidence of degradation of peak resolution, a shift in the calibration curve, loss of sensitivity, or failure to continually meet one of the quality control criteria.

Scheduled routine maintenance is defined in each method SOP. It is the responsibility of each Technical Manager to ensure that instrument maintenance logs are kept for all equipment in his/her department. Preventative maintenance procedures are also outlined in analytical SOPs or instrument manuals. (Note: for some equipment, the log used to monitor performance is also the maintenance log. Multiple pieces of equipment may share the same log as long as it is clear as to which instrument is associated with an entry.)

Instrument maintenance logs are controlled and are used to document instrument problems, instrument repair and maintenance activities. Maintenance logs shall be kept for all major pieces of equipment. Instrument maintenance logs may also be used to specify instrument parameters.

- Documentation must include all major maintenance activities such as contracted preventive maintenance and service and in-house activities such as the replacement of electrical components, lamps, tubing, valves, columns, detectors, cleaning and adjustments.
- Each entry in the instrument log includes the analyst's initials, the date, a detailed description of the problem (or maintenance needed/scheduled), a detailed explanation of the solution or maintenance performed, and a verification that the equipment is functioning properly (state what was used to determine a return to control. e.g. CCV run on *'date'* was acceptable, or instrument recalibrated on 'date' with acceptable verification, etc.) must also be documented in the instrument records.
- When maintenance or repair is performed by an outside agency, service receipts detailing the service performed can be affixed into the logbooks adjacent to pages describing the maintenance performed. This stapled in page must be signed across the page entered and the logbook so that it is clear that a page is missing if only half a signature is found in the logbook.

If an instrument requires repair (subjected to overloading or mishandling), gives suspect results, or otherwise has shown to be defective or outside of specified limits it shall be taken out of operation and tagged as out-of-service or otherwise isolated until such a time as the repairs have been made and the instrument can be demonstrated as operational by calibration and/or verification or other test to demonstrate acceptable performance. The laboratory shall examine the effect of this defect on previous analyses.

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In the event of equipment malfunction that cannot be resolved, service shall be obtained from the instrument vendor manufacturer, or qualified service technician, if such a service can be tendered. If on-site service is unavailable, arrangements shall be made to have the instrument shipped back to the manufacturer for repair. Back up instruments, which have been approved, for the analysis shall perform the analysis normally carried out by the malfunctioning instrument. If the back-up is not available and the analysis cannot be carried out within the needed timeframe, the samples shall be subcontracted.

At a minimum, if an instrument is sent out for service or transferred to another facility, it must be recalibrated and the laboratory MDL verified (using an MDLV) prior to return to lab operations.

18.3) Support Equipment

This section applies to all devices that may not be the actual test instrument, but are necessary to support laboratory operations. These include but are not limited to: balances, ovens, refrigerators, freezers, incubators, water baths, temperature measuring devices, thermal/pressure sample preparation devices and volumetric dispensing devices if quantitative results are dependent on their accuracy, as in standard preparation and dispensing or dilution into a specified volume. All raw data records associated with the support equipment are retained to document instrument performance.

18.3.1) Weights and Balances

The accuracy of the balances used in the laboratory is checked every working day, before use. All balances are placed on stable counter tops.

Each balance is checked prior to initial serviceable use with at least two certified ASTM type 1 weights spanning its range of use (weights that have been calibrated to ASTM type 1 weights may also be used for daily verification). ASTM type 1 weights used only for calibration of other weights (and no other purpose) are inspected for corrosion, damage or nicks at least annually and if no damage is observed, they are calibrated at least every 5 years by an outside calibration laboratory. Any weights (including ASTM Type 1) used for daily balance checks or other purposes are recalibrated/recertified annually to NIST standards (this may be done internally if laboratory maintains "calibration only" ASTM type 1 weights).

All balances are serviced annually by a qualified service representative, who supplies the laboratory with a certificate that identifies traceability of the calibration to the NIST standards.

All of this information is recorded in logs, and the recalibration/recertification certificates are kept on file. (*EFGS-Q-QD-SOP2710*, Class 1 Weight Calibration, Balance Verification, Calibration & Maintenance)

18.3.2) pH, Conductivity, and Turbidity Meters

The pH meters used in the laboratory are accurate to + 0.1 pH units, and have a scale readability of at least 0.05 pH units. The meters automatically compensate for the temperature, and are calibrated with at least two working range buffer solutions before each use.

Conductivity meters used in the laboratory are capable or measuring conductivity with an error not exceeding 1% or one umhos/cm, whichever is greater. The meters are also calibrated before each use with a known standard.

Turbidity meters are also calibrated before each use. All of this information is documented in logs.

Consult pH, Conductivity, and Turbidity SOPs for further information.

18.3.3) Thermometers

All thermometers are calibrated on an annual basis with a NIST-traceable thermometer.

- If the temperature measuring device is used over a range of 10°C or less, then a single point verification within the range of use is acceptable;
- If the temperature measuring device is used over a range of greater than 10°C, then the verification must bracket the range of use.

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IR thermometers, digital probes and thermocouples are calibrated quarterly. IR Thermometers should be calibrated over the full range of use, including ambient, iced (4°C) and frozen (0°C to -5°C), per the Drinking Water Manual.

The mercury/digital NIST thermometers are recalibrated every five years/one year (unless thermometer has been exposed to temperature extremes or apparent separation of internal liquid) by an approved outside service and the provided certificate of traceability is kept on file. The NIST thermometer(s) have increments of 1 degree, and have ranges applicable to method and certification requirements. The NIST traceable thermometers are used for no other purpose than to calibrate other thermometers.

All of this information is documented in logbooks. Monitoring method-specific temperatures, including incubators, heating blocks, water baths, and ovens, is documented in method-specific logbooks. More information on this subject can be found in the Use, Calibration, and Maintenance of Laboratory Thermometers and Refrigerator and Freezer Temperature Monitoring and Maintenance SOP *EFGS-Q-QD-SOP2831*.

18.3.4) Refrigerators/Freezer Units, Water baths, Ovens and Incubators

The temperatures of all refrigerator units and freezers used for sample and standard storage are monitored each working day. (Sample storage for DoD/DOE samples is monitored 7 days a week).

Ovens, water baths and incubators are monitored on days of use.

All of this equipment has a unique identification number, and is assigned a thermometer for monitoring.

Sample storage refrigerator temperatures are kept between > 0ºC and < 6 ºC.

Specific temperature settings/ranges for other refrigerators, ovens, water baths, and incubators can be found in method specific SOPs.

All of this information is documented in Daily Temperature Logbooks and method-specific logbooks.

18.3.5) Autopipettors, Dilutors, and Syringes

Mechanical volumetric dispensing devices including burettes (except Class A Glassware and glass microliter syringes) are given unique identification numbers and the delivery volumes are verified gravimetrically, at a minimum, on a quarterly basis (daily for DoD/DOE projects).

For those dispensers that are not used for measurements, a label shall be applied to the device stating that it is not calibrated. Any device not regularly verified cannot be used for any quantitative measurements.

Micro-syringes are purchased from Hamilton Company. Each syringe is traceable to NIST. The laboratory keeps on file an "Accuracy and Precision Statement of Conformance" from Hamilton attesting established accuracy.

18.4) Instrument Calibrations

Calibration of analytical instrumentation is essential to the production of quality data. Strict calibration procedures are followed for each method. These procedures are designed to determine and document the method detection limits, the working range of the analytical instrumentation and any fluctuations that may occur from day to day.

Sufficient raw data records are retained to allow an outside party to reconstruct all facets of the initial calibration. Records contain, but are not limited to, the following: calibration date, method, instrument, analyst(s) initials or signatures, analysis date, analytes, concentration, response, and type of calibration (Avg RF, curve, or other calculations that may be used to reduce instrument responses to concentration.)

Sample results must be quantitated from the initial calibration and may not be quantitated from any continuing instrument calibration verification unless otherwise required by regulation, method or program.

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If the initial calibration results are outside of the acceptance criteria, corrective action is performed and any affected samples are reanalyzed if possible. If the reanalysis is not possible, any data associated with an unacceptable initial calibration will be reported with appropriate data qualifiers (refer to Section 12).

Note: Instruments are calibrated initially and as needed after that and at least annually.

18.4.1) Calibration Standards

Calibration standards are prepared using the procedures indicated in the Reagents and Standards section of the determinative method SOP. If a reference method does not specify the number of calibration standards, a minimum of 3 calibration points will be used.

Standards for instrument calibration are obtained from a variety of sources. All standards are traceable to national or international standards of measurement, or to national or international standard reference materials.

The lowest concentration calibration standard that is analyzed during an initial calibration must be at or below the stated reporting limit for the method based on the final volume of extract (or sample).

The other concentrations define the working range of the instrument/method or correspond to the expected range of concentrations found in actual samples that are also within the working range of the instrument/method. Results of samples not bracketed by initial instrument calibration standards (within calibration range to at least the same number of significant figures used to report the data) must be reported as having less certainty, e.g., defined qualifiers or flags (additional information may be included in the case narrative). The exceptions to these rules. ICP and ICPMS methods which define the working range with periodic linear dynamic range studies, rather than through the range of concentrations of daily calibration standards.

All initial calibrations are verified with a standard obtained from a second source and traceable to a national standard, when available (or vendor certified different lot if a second source is not available). For unique situations, such as air analysis where no other source or lot is available, a standard made by a different analyst at a different time or a different preparation would be considered a second source. This verification occurs immediately after the calibration curve has been analyzed, and before the analysis of any samples.

18.4.1.1 Calibration Verification

The calibration relationship established during the initial calibration must be verified initially and at least daily as specified in the laboratory method SOPs in accordance with the referenced analytical methods and in the 2009 and 2016 TNI Standard. The process of calibration verification applies to both external standard and internal standard calibration techniques, as well as to linear and non-linear calibration models. Initial calibration verification (ICV) is with a standard source secondary (second source standard) to the calibration standards, but continuing calibration verifications (CCV) may use the same source standards as the calibration curve.

Note: The process of calibration verification referred to here is fundamentally different from the approach called "calibration" in some methods. As described in those methods, the calibration factors or response factors calculated during calibration are used to update the calibration factors or response factors used for sample quantitation. This approach, while employed in other EPA programs, amounts to a daily single-point calibration.

All target analytes and surrogates, including those reported as non-detects, must be included in periodic calibration verifications for purposes of retention time confirmation and to demonstrate that calibration verification criteria are being met, i.e., RPD, per 2009 and 2016 TNI Std. EL-V1M4 Sec. 1.7.2.

All samples must be bracketed by periodic analyses of standards that meet the QC acceptance criteria (e.g., calibration and retention time). The frequency is found in the determinative methods or SOPs.

Note: If an internal standard calibration is being used then bracketing calibration verification standards may not be are not required, only daily verifications are needed. The results from these

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verification standards must meet the calibration verification criteria and the retention time criteria (if applicable).

Generally, the calibrations must be verified by an ICV analyzed immediately following initial calibration and before sample analysis. The ICV may be used as the first bracketing CCV, if criteria for both are met.

A continuing instrument calibration verification (CCV) is generally analyzed at the beginning of each 12-hour analytical shift during which samples are analyzed. The 12-hour analytical shift begins with the injection of the calibration verification standard (or the MS tuning standard in MS methods). The shift ends after the completion of the analysis of the last sample, QC, or standard that can be injected within 12-hours of the beginning of the shift. For methods that have quantitation by external calibration models, a CCV is analyzed at the end of each analytical sequence. Some methods have more frequent CCV requirements. See specific SOPs. Most inorganic methods require the CCV to be analyzed after ever 10 samples or injections, including matrix or batch QC samples.

Note: If an internal standard calibration is being used (e.g., GCMS) then bracketing standards are not required, only daily verifications are needed, except as specified by program or method requirements.

If the results of a CCV are outside the established acceptance criteria and analysis of a second consecutive (and immediate) CCV fails to produce results within acceptance criteria, corrective action shall be performed. Once corrective actions have been completed and documented, the laboratory shall demonstrate acceptable instrument / method performance by analyzing two consecutive CCVs, or a new initial instrument calibration shall be performed.

Sample analyses and reporting of data may not occur or continue until the analytical system is calibrated or calibration verified. However, data associated with an unacceptable calibration verification may be fully useable reported based upon discussion and approval of the client under the following special conditions:

a). when the acceptance criteria for the CCV are exceeded high (i.e., high bias) and the associated samples within the batch are non-detects, then those non-detects may be reported case narrative comment explaining the high bias. Otherwise the samples affected by the unacceptable CCV shall be re-analyzed after a new calibration curve has been established, evaluated and accepted; or

b). when the acceptance criteria for the CCV are exceeded low (i.e., low bias), those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable CCV shall be re-analyzed after a new calibration curve has been established, evaluated and accepted.

Samples reported by the 2 conditions identified above will be appropriately flagged.

18.4.1.2 Verification of Linear and Non-Linear Calibrations

Calibration verification for calibrations involves the calculation of the percent drift or the percent difference of the instrument response between the initial calibration and each subsequent analysis of the verification standard. (These calculations are available in the laboratory method SOPs.) Verification standards are evaluated based on the % Difference from the average CF or RF of the initial calibration or based on % Drift or % Recovery if a linear or quadratic curve is used.

Regardless of whether a linear or non-linear calibration model is used, if initial verification criterion is not met, then no sample analyses may take place until the calibration has been verified or a new initial calibration is performed that meets the specifications listed in the method SOPs. If the calibration cannot be verified after the analysis of a single verification standard, then adjust the instrument operating conditions and/or perform instrument maintenance, and analyze another aliquot of the verification standard. If the calibration cannot be verified with the second standard, then a new initial calibration is performed.

- When the acceptance criteria for the calibration verification are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise, the samples affected by the unacceptable calibration verification shall be reanalyzed after a new calibration curve has been established, evaluated and accepted.

- When the acceptance criteria for the calibration verification are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise, the samples affected by the unacceptable verification shall be reanalyzed after a new calibration curve has been established, evaluated and accepted. Alternatively, a reporting limit standard may be analyzed to demonstrate that the laboratory can still support non-detects at their reporting limit.

18.5) Tentatively Identified Compounds (TICs) – GC/MS Analysis

For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Additional details are provided in NDSC Document No. CA-Q-QM-001, Tentatively Identified Compounds (TICS) - GCMS Analysis.

Note: If the TIC compound is not part of the client target analyte list but is calibrated by the laboratory and is both qualitatively and/or quantitatively identifiable, it should not be reported as a TIC. If the compound is reported on the same form as true TICs, it should be qualified and/or narrated that the reported compound is qualitatively and quantitatively (if verification in control) reported compared to a known standard that is in control (where applicable).

18.6) GC/MS Tuning

Prior to any GC/MS analytical sequence, including calibration, the instrument parameters for the tune and subsequent sample analyses within that sequence must be set.

Prior to tuning/auto-tuning the mass spectrometer, the parameters may be adjusted within the specifications set by the manufacturer or the analytical method. These generally do not need any adjustment but it may be required based on the current instrument performance. If the tune verification does not pass it may be necessary to clean the source or perform additional maintenance. Any maintenance is documented in the maintenance log.

18.6) Table 18-1. Example – Instrumentation List

GC	GC/MS	ICP	ICPMS	CVAA	AutoAnalyzer	IC	TOC
13	15	1	2	4	2	2	2

19) MEASUREMENT TRACEABILITY

19.1) Overview

Traceability of measurements shall be assured using a system of documentation, calibration, and analysis of reference standards. Laboratory equipment that are peripheral to analysis and whose calibration is not necessarily documented in a test method analysis or by analysis of a reference standard shall be subject to ongoing certifications of accuracy. At a minimum, these must include procedures for checking specifications of ancillary equipment: balances, thermometers, temperature, Deionized (DI) and Reverse Osmosis (RO) water systems, automatic pipettes and other volumetric measuring devices. (Refer to Section 18.3). With the exception of Class A Glassware and glass microliter syringes, quarterly accuracy checks are performed for all mechanical volumetric devices. Micro syringes are verified at least semi-annually or disposed of after 6 months of use. Wherever possible, subsidiary or peripheral equipment is checked against standard equipment or standards that are traceable to national or international standards. Class A Glassware and glass microliter syringes should be routinely inspected for chips, acid etching or deformity (e.g., bent needle). If the Class A glassware or syringe is suspect, the accuracy of the glassware will be assessed prior to use.

19.2) NIST-Traceable Weights and Thermometers

Reference standards of measurement shall be used for calibration only and for no other purpose, unless it can be shown that their performance as reference standards would not be invalidated.

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For NIST-traceable weights and thermometers, the laboratory requires that all calibrations be conducted by a calibration laboratory accredited by A2LA, NVLAP (National Voluntary Laboratory Accreditation Program), or another accreditation organization that is a signatory to a MRA (Mutual Recognition Arrangement) of one or more of the following cooperations – ILAC (International Laboratory Accreditation Cooperation) or APLAC (Asia–Pacific Laboratory Accreditation Cooperation). A calibration certificate and scope of accreditation is kept on file at the laboratory.

19.3) Reference Standards / Materials

Reference standards/materials, where commercially available, are traceable to certified reference materials. Commercially prepared reference standards, to the extent available, are purchased from vendors that are accredited to ISO Guide 34 and ISO/IEC Guide 17025. All reference standards from commercial vendors shall be accompanied with a certificate that includes at least the following information:

- Manufacturer
- Analytes or parameters calibrated
- Identification or lot number
- Calibration method
- Concentration with associated uncertainties
- Purity

If a standard cannot be purchased from a vendor that supplies a Certificate of Analysis, the purity of the standard is documented by analysis. The receipt of all reference standards must be documented. Reference standards are labeled with a unique Standard Identification Number and expiration date. All documentation received with the reference standard is retained as a QC record and references the Standard Identification Number.

All reference, primary and working standards/materials, whether commercially purchased or laboratory prepared, must be checked regularly to ensure that the variability of the standard or material from the true value does not exceed method requirements. The accuracy of calibration standards is checked by comparison with a standard from a second source. In cases where a second standard manufacturer is not available, a vendor certified different lot is acceptable for use as a second source. The appropriate Quality Control (QC) criteria for specific standards are defined in laboratory SOPs. In most cases, the analysis of an Initial Calibration Verification (ICV) or LCS (where there is no sample preparation) is used as the second source confirmation. These checks are generally performed as an integral part of the analysis method (e.g. calibration checks, laboratory control samples).

All standards and materials must be stored and handled according to method or manufacturer's requirements in order to prevent contamination or deterioration. Refer to the Environmental Health & Safety Manual or laboratory SOPs. For safety requirements, please refer to method SOPs and the laboratory's Chemical Hygiene Plan.

Standards and reference materials shall not be used after their expiration dates unless their reliability is verified by the laboratory and their use is approved by the Quality Assurance Manager. The laboratory must have documented contingency procedures for re-verifying expired standards.

19.4) Documentation and Labeling of Standards, Reagents, and Reference Materials

Reagents must be at a minimum the purity required in the test method. The date of reagent receipt and the expiration date are documented. The lots for most of the common solvents and acids are tested for acceptability prior to company-wide purchase. [Refer to NDSC Document No. CA-Q-S-001, Solvent and Acid Lot Testing and Approval]

All manufacturer or vendor supplied Certificate of Analysis or Purity must be retained, stored appropriately, and readily available for use and inspection. These records are scanned and appended to the standard record in the LIMS. Records must be kept of the date of receipt and date of expiration of standards, reagents and reference materials. In addition, records of preparation of laboratory standards, reagents, and reference materials must be retained, stored appropriately, and be readily available for use and inspection. For detailed information on documentation and labeling, please refer to SOP *EFGS-T-TM-SOP2839*, "Stock and Working Standards for Trace Metals" and *EFGS-Q-QD-SOP41922* "Receipt, Preparation, Storage and Verification of Standards and Reagents and Traceability Protocols".

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Commercial materials purchased for preparation of calibration solutions, spike solutions, etc.., are usually accompanied with an assay certificate or the purity is noted on the label. If the assay purity is 96% or better, the weight provided by the vendor may be used without correction. If the assay purity is less than 96% a correction will be made to concentrations applied to solutions prepared from the stock commercial material. Blended gas standard cylinders use a nominal concentration if the certified value is within +/-15%, otherwise the certified values is used for the canister concentration.

19.4.1 All standards, reagents, and reference materials must be labeled in an unambiguous manner. Standards are logged into the laboratory's LIMS, and are assigned a unique identification number. The following information is typically recorded in the electronic database within the LIMS.

- Standard ID
- Description of Standard
- Department
- Preparer's name
- Final volume and number of vials prepared
- Solvent type and lot number
- Preparation Date
- Expiration Date
- Standard source type (stock or daughter)
- Standard type (spike, surrogate, other)
- Parent standard ID (if applicable)
- Parent Standard Analyte Concentration (if applicable)
- Parent Standard Amount used (if applicable)
- Component Analytes
- Final concentration of each analyte
- Comment box (text field)

Records are maintained electronically for standard and reference material preparation. These records show the traceability to purchased stocks or neat compounds. These records also include method of preparation, date of preparation, expiration date and preparer's name or initials. Preparation procedures are provided in the Method SOPs.

19.4.2 All standards, reagents, and reference materials must be clearly labeled with a minimum of the following information:

- Expiration Date (include prep date for reagents)
- Standard ID from LIMS
- Special Health/Safety warnings if applicable

Records must also be maintained of the date of receipt for commercially purchased items or date of preparation for laboratory prepared items. Special Health/Safety warnings must also be available to the analyst. This information is maintained by the EH&S Officer.

19.4.3 In addition, the following information may be helpful:

- Date opened (for multi-use containers, if applicable)
- Description of standard (if different from manufacturer's label or if standard was prepared in the laboratory)
- Recommended Storage Conditions
- Concentration (if applicable)
- Initials of analyst preparing standard or opening container

All containers of prepared reagents must include an expiration date and an ID number to trace back to preparation.

Procedures for preparation of reagents can be found in the Method SOPs.

Standard ID numbers must be traceable through associated logbooks, worksheets and preparation/analytical batch records.

All reagents and standards must be stored in accordance to the following priority: 1) with the manufacturer's recommendations; 2) with requirements in the specific analytical methods as specified in the laboratory SOP.

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20) SAMPLING

20.1) Overview

The laboratory does not provide sampling services. The laboratory's responsibility in the sample collection process lies in supplying the sampler with the necessary coolers, reagent water, sample containers, preservatives, sample labels, custody seals, COC forms, ice, and packing materials required to properly preserve, pack, and ship samples to the laboratory

20.2) Sampling Containers

The laboratory offers clean sampling containers for use by clients. These containers are obtained from reputable container manufacturers and meet EPA specifications as required. Certificates of cleanliness for bottles and preservatives are provided by the supplier and are maintained at the laboratory. Alternatively, the certificates may be maintained by the supplier and available to the laboratory on-line.

20.2.1) Preservatives

Upon request, preservatives are provided to the client in pre-cleaned sampling containers. In some cases containers may be purchased pre-preserved from the container supplier. Whether prepared by the laboratory or bought pre-preserved, the grades of the preservatives are at a minimum:

- Hydrochloric Acid – Reagent ACS (Certified VOA Free) or equivalent
- Methanol – Purge and Trap grade
- Nitric Acid – Instra-Analyzed or equivalent
- Sodium Bisulfate – ACS Grade or equivalent
- Sodium Hydroxide – Instra-Analyzed or equivalent
- Sulfuric Acid – Instra-Analyzed or equivalent
- Sodium Thiosulfate – ACS Grade or equivalent

20.3) Definition of Holding Time

The date and time of sampling documented on the COC form establishes the day and time zero. As a general rule, when the maximum allowable holding time is expressed in days (e.g., 14 days, 28 days), the holding time is based on calendar day measured. Holding times expressed in hours (e.g., 6 hours, 24 hours, etc.) are measured from date and time zero. Holding times for analysis include any necessary reanalysis. However, there are some programs that determine holding time compliance based on the date and specific time of analysis compared to the time of sampling regardless of how long the holding time is.

20.4) Sampling Containers, Preservation Requirements, Holding Times

The preservation and holding time criteria specified in the laboratory SOPs are derived from the source documents for the methods. If method required holding times or preservation requirements are not met, the reports will be qualified using a flag, footnote or case narrative. As soon as possible or "ASAP" is an EPA designation for tests for which rapid analysis is advised, but for which neither EPA nor the laboratory have a basis for a holding time.

20.5) Sample Aliquots / Subsampling

Taking a representative sub-sample from a container is necessary to ensure that the analytical results are representative of the sample collected in the field. The size of the sample container, the quantity of sample fitted within the container, and the homogeneity of the sample need consideration when sub-sampling for sample preparation. It is the laboratory's responsibility to take a representative subsample or aliquot of the sample provided for analysis.

Analysts should handle each sample as if it is potentially dangerous. At a minimum, safety glasses, gloves, and lab coats must be worn when preparing aliquots for analysis.

Guidelines on taking sample aliquots and subsampling are located SOP # *EFGS-P-SP-SOP5147*.

21) HANDLING OF SAMPLES

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It is the responsibility of the client to send us representative and/or homogeneous and properly preserved samples of the system from which they are drawn. The laboratory assumes that all multiple sample containers with the same designator/description and bottle type contain a homogeneous, representative sample.

The laboratory provides the appropriate sample containers, required preservative, chain-of-custody (COC) forms, shipping containers, labels, and custody seals. The laboratory also provides trip blanks and analyte-free water for field blanks. Preparation of methanol containers for field preservation of volatile soil samples is available.

Sample management procedures at the laboratory ensure that sample integrity and custody are maintained and documented from sampling/receipt through disposal.

21.1) Chain of Custody (COC)

The COC form is the written documented history of any sample and is initiated when bottles are sent to the field, or at the time of sampling. This form is completed by the sampling personnel and accompanies the samples to the laboratory where it is received and stored under the laboratory's custody. The purpose of the COC form is to provide a legal written record of the handling of samples from the time of collection until they are received at the laboratory. It also serves as the primary written request for analyses from the client to the laboratory. The COC form acts as a purchase order for analytical services when no other contractual agreement is in effect.

21.1.1) Field Documentation

The information the sampler needs to provide at the time of sampling on the container label is:

- Sample identification
- Date and time
- Preservative

During the sampling process, the COC form is completed and must be legible. This form includes information such as:

- Client name, address, phone number and fax number (if available)
- Project name and/or number
- The sample identification
- Date, time and location of sampling
- Sample collectors name
- The matrix description
- The container description
- The total number of each type of container
- Preservatives used
- Analysis requested
- Requested turnaround time (TAT)
- Any special instructions
- Purchase Order number or billing information (e.g. quote number) if available
- The date and time that each person received or relinquished the sample(s), including their signed name.

When the sampling personnel deliver the samples directly to the laboratory personnel, the samples are stored in a cooler with ice, as applicable, and remain solely in the possession of the client's field technician until the samples are delivered to the laboratory personnel. The sample collector must assure that each container is in his/her physical possession or in his/her view at all times, or stored in such a place and manner to preclude tampering. The field technician relinquishes the samples in writing on the COC form to the sample control personnel at the laboratory or to a laboratory courier. When sampling personnel deliver the samples through a common carrier (Fed-Ex, UPS), the CoC relinquished date/time is completed by the field personnel and samples are released to the carrier. Samples are only considered to be received by the laboratory when personnel at the fixed laboratory facility have physical contact with the samples.

Note: Independent couriers are not required to sign the COC form. The COC is usually kept in the sealed sample cooler. The receipt from the courier is stored in log-in by date; it lists all receipts each date.

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21.1.2) Legal / Evidentiary Chain-of-Custody

If samples are identified for legal/evidentiary purposes on the COC, login will complete the custody seal retain the shipping record with the COC, and initiate an internal COC for laboratory use by analysts and a sample disposal record.

21.2) Sample Receipt

Samples are received at the laboratory by designated sample receiving personnel and a unique laboratory project identification number is assigned. Each sample container shall be assigned a unique sample identification number that is cross-referenced to the client identification number such that traceability of test samples is unambiguous and documented. Each sample container is affixed with a durable sample identification label. Sample acceptance, receipt, tracking and storage procedures are detailed in the laboratory's SOP No. *EFGS-P-SH-SOP41445* "Sample Receipt and Log-in Using TALS LIMS" and *EFGS-P-SH-SOP2793*, "Shipping and Receiving of Client Samples Using Element LIMS" and summarized in the following sections.

21.2.1) Laboratory Receipt

When samples arrive at the laboratory, sample receiving personnel inspect the coolers and samples. The integrity of each sample must be determined by comparing sample labels or tags with the COC and by visual checks of the container for possible damage. Any non-conformance, irregularity, or compromised sample receipt must be documented on the Sample Receipt Checklist and brought to the immediate attention of the client. The COC, shipping documents, documentation of any non-conformance, irregularity, or compromised sample receipt, record of client contact, and resulting instructions become part of the project record.

Sample Registration personnel check and document preservation of non-volatile liquid samples after the samples have been entered into the LIMS and before they are released to the laboratory for testing or placed into storage.

21.3) Sample Acceptance Policy

The laboratory has a written sample acceptance policy (Figure 21-1) that clearly outlines the circumstances under which samples shall be accepted or rejected. These include:

- a COC filled out completely;
- samples must be properly labeled;
- proper sample containers with adequate volume for the analysis (Sampling Guide) and necessary QC;
- samples must be preserved according to the requirements of the requested analytical method (Sampling Guide);
- Client must notify the lab of any potentially hazardous samples;
- Client must notify the lab of any samples from potentially radioactive sites, the samples must by surveyed for radioactive prior to shipment to the lab and the results of this radioassay must accompany the sample.
- sample holding times must be adhered to (Sampling Guide);
- the project manager will be notified if any sample is received in damaged condition.

Data from samples which do not meet these criteria are flagged and the nature of the variation from policy is defined.

21.3.1 After inspecting the samples, the sample receiving personnel sign and date the COC form, make any necessary notes of the samples' conditions and store them in appropriate refrigerators or storage locations.

21.3.2 Any deviations from these checks that question the suitability of the sample for analysis, or incomplete documentation as to the tests required will be resolved by consultation with the client. If the sample acceptance policy criteria are not met, the laboratory shall either:

- Retain all correspondence and/or records of communications with the client regarding the disposition of rejected samples, or
- Fully document any decision to proceed with sample analysis that does not meet sample acceptance criteria.

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Once sample acceptance is verified, the samples are logged into LIMS according SOP No. *EFGS-P-SH-SOP41445* or *EFGS-P-SH-SOP2793*.

21.4) Sample Storage

In order to avoid deterioration, contamination or damage to a sample during storage and handling, from the time of receipt until all analyses are complete, samples are stored in refrigerators, freezers or protected locations suitable for the sample matrix. Water samples for ICP or ICPMS analysis are stored on ambient storage shelves. Samples are never to be stored with reagents, standards or materials that may create contamination.

Analysts and technicians retrieve the sample container allocated to their analysis from the designated storage location and place them on carts, analyze the sample, and return the remaining sample or empty container to the storage location from which it originally came. All samples are kept in the storage locations until approved for disposal by the PM.

Access to the laboratory is controlled such that sample storage need not be locked at all times unless a project specifically demands it. Samples are accessible to laboratory personnel only. Visitors to the laboratory are prohibited from entering the refrigerator and laboratory areas unless accompanied by an employee of Eurofins Seattle.

21.5) Hazardous Samples and Foreign Soils

To minimize exposure to personnel and to avoid potential accidents, hazardous and foreign soil samples are stored in an isolated area designated for hazardous waste or foreign soil samples only. All hazardous samples are either returned to the client or disposed of appropriately through a hazardous waste disposal firm that lab-packs all hazardous samples and removes them from the laboratory. Foreign soil samples are sent out for incineration by a USDA-approved waste disposal facility.

21.6) Sample Shipping

In the event that the laboratory needs to ship samples, the samples are placed in a cooler with enough ice to ensure the samples remain just above freezing and at or below 6.0°C during transit. The samples are carefully surrounded by packing material to avoid breakage (yet maintain appropriate temperature). A trip blank is enclosed for those samples requiring water/solid volatile organic analyses (see Note). The chain-of-custody form is signed by the sample control technician and attached to the shipping paperwork. Samples are generally shipped overnight express or hand-delivered by a Eurofins Seattle courier to maintain sample integrity. All personnel involved with shipping and receiving samples must be trained to maintain the proper chain-of-custody documentation and to keep the samples intact and on ice. The laboratory's Chemical Hygiene Plan contains additional shipping requirements.

Note: If a client does not request trip blank analysis on the COC or other paperwork, the laboratory will not analyze the trip blanks that were supplied. However, in the interest of good client service, the laboratory will advise the client at the time of sample receipt that it was noted that they did not request analysis of the trip blank; and that the laboratory is providing the notification to verify that they are not inadvertently omitting a key part of regulatory compliance testing.

21.7) Sample Disposal

Samples should be retained for a minimum of 30 days after the project report is sent, however, provisions may be made for earlier disposal of samples once the holding time is exceeded. Some samples are required to be held for longer periods based on regulatory or client requirements (e.g., 60 days after project report is sent). The laboratory must follow the longer sample retention requirements where required by regulation or client agreement. Several possibilities for sample disposal exist: the sample may be consumed completely during analysis, the sample may be returned to the customer or location of sampling for disposal, or the sample may be disposed of in accordance with the laboratory's waste disposal procedures (SOP: *EFGS-S-HS-SOP2991*). All procedures in the laboratory's Chemical Hygiene Plan are followed during disposal. Samples are normally maintained in the laboratory no longer than 90 days from receipt unless otherwise requested. Unused portions of samples found or suspected to be hazardous according to state or federal guidelines may be returned to the client upon completion of the analytical work.

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If a sample is part of a known litigation, the affected legal authority, sample data user, and/or submitter of the sample must participate in the decision about the sample's disposal. All documentation and correspondence concerning the disposal decision process must be kept on file. Pertinent information includes the date of disposal, nature of disposal (such as sample depletion, hazardous waste facility disposal, return to client), names of individuals who conducted the arrangements and physically completed the task. The laboratory will remove or deface sample labels prior to disposal unless this is accomplished through the disposal method (e.g., samples are incinerated). A Waste Disposal Record should be completed.

21.7) Figure 23-1. Example: Sample Acceptance Policy

All incoming work will be evaluated against the criteria listed below. Where applicable, data from any samples that do not meet the criteria listed below will be noted on the laboratory report defining the nature and substance of the variation. In addition the client will be notified either by telephone, fax or e-mail ASAP after the receipt of the samples.

Per State and/or Federal Regulation, the client is responsible to ensure that samples are shipped in accordance with DOT/IATA requirements, and that radioactive materials may only be delivered to licensed facilities. Any samples containing (or suspected to contain) Source, Byproduct, or Special Nuclear Material as defined by 10 CFR should be delivered directly to facilities licensed to handle such radioactive material. Natural material or ores containing naturally occurring radionuclides may be delivered to any Eurofins Seattle facility or courier as long as the activity concentration of the material does not exceed 270 pCi/g alpha or 2700 pCi/g beta (49 CFR Part 173).

1) Chain of Custody

The Chain of Custody should include:

- Client name, address, phone number and fax number (if available)
- Project name and/or number
- Samplers' initials
- Project Location
- Unique sample identifier
- Date and time of sample collection
- Requested analytes and methods
- The matrix description
- Field preservation (when samples are preserved prior to receipt at EFGS)
- The total number of each type of container
- Requested turnaround time (TAT)
- Purchase Order number or billing information (e.g. quote number) if available
- Any special instructions concerning the samples
- The date and time that each person received or relinquished the sample(s), including their signed name.
- Information must be legible

If the Chain of Custody is incomplete, the EFGS project manager may reject the samples.

2) Sample Container Labeling

- The sample containers must be labeled with a unique sample ID (if EFGS supplied the bottles, this may be the EFGS bottle ID).
- The label must be water-resistant and any information on It must be in indelible ink or printing.
- Include sampling date and time
- Include preservative used.
- Information must be legible

3) Sample Volume

- The client must submit adequate volume for the analysis requested.
- The EFGS form "Bottle Types, Preservation, and Handling Instructions" lists volumes required.
- If insufficient sample volume is received, sample dilution may be required. Sample dilution will elevate the reporting limit(s) for the sample results.

4) Health & Safety

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- It is the responsibility of the client to alert the EFGS project manager if the samples are potentially hazardous. All samples know or suspected to be very high in trace metals (or any other hazardous constituents) must be so identified by the client.
- Samples fro potentially radioactive sites must be surveyed for radioactivity before shipment to EFGS. The results of this radioassay must accompany the samples, and EFGS must be notified as to when these samples are expected to arrive.

Failure to follow these safety precautions may results in additional charges, return of the samples, or possible liability for damages or injuries that results

5) Most analytical methods require chilling samples to 4° C (other than water samples for EPA 200.8 metals analysis). For these methods, the criteria are met if the samples are chilled to below 6o C and above freezing (0oC).

5i.) Samples that are delivered to the laboratory on the same day they are collected may not meet the requirements of Section 5. In these cases, the samples shall be considered acceptable if the samples were received on ice.

5ii.) If sample analysis is begun within fifteen (15) minutes of collection, thermal preservation is not required.

5iii.)Thermal preservation is not required in the field if the laboratory receives and refrigerates the sample within fifteen (15) minutes of collection.

- Chemical preservation (pH) will be verified prior to analysis and documented, either in sample control or at the analyst's level. The project manager will be notified immediately if there is a discrepancy. If analyses will still be performed, all affected results will be flagged to indicate

Sample Holding Times

- Eurofins Seattle will make every effort to analyze samples within the regulatory holding time. Samples must be received in the laboratory with enough time to perform the sample analysis. Except for short holding time samples (< 48hr HT) sample must be received with at least 48 hrs (2 working days) remaining on the holding time for us to ensure analysis.

6) The project manager will be notified if any sample is received in damaged condition. Eurofins Seattle will request that a sample be resubmitted for analysis.

7) Recommendations for packing samples for shipment.

- Pack samples in Ice rather than "Blue" ice packs.
- Soil samples should be placed in plastic zip-lock bags. The containers often have dirt around the top and do not seal very well and are prone to intrusion from the water from melted ice.
- Water samples would be best if wrapped with bubble-wrap or paper (newspaper, or paper towels work) and then placed in plastic zip-lock bags.
- Fill extra cooler space with bubble wrap.

22) ASSURING THE QUALITY OF TEST RESULTS

22.1) Overview

In order to assure our clients of the validity of their data, the laboratory continuously evaluates the quality of the analytical process. The analytical process is controlled not only by instrument calibration as discussed in Section 20, but also by routine process quality control measurements (e.g. Blanks, Laboratory Control Samples (LCS), Matrix Spikes (MS), duplicates (DUP), surrogates, Internal Standards (IS)). These quality control checks are performed as required by the method or regulations to assess precision and accuracy. Quality control samples are to be treated in the exact same manner as the associated field samples being tested. In addition to the routine process quality control samples, Proficiency Testing (PT) Samples (concentrations unknown to laboratory) are analyzed to help ensure laboratory performance.

22.2) Controls

Sample preparation or pre-treatment is commonly required before analysis. Typical preparation steps include homogenization, grinding, acid digestion and drying. During these pre-treatment steps, samples are arranged into discreet manageable groups referred to as preparation (prep)

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batches. Prep batches provide a means to control variability in sample treatment. Control samples are added to each prep batch to monitor method performance and are processed through the entire analytical procedure with investigative/field samples.

22.3) Negative Controls

22.3) Table 22-1. Example – Negative Controls

Control Type	Details
Method Blank (MB)	are used to assess preparation and analysis for possible contamination during the preparation and processing steps.
	The specific frequency of use for method blanks during the analytical sequence is defined in the specific standard operating procedure for each analysis. Generally it is 1 for each batch of samples; not to exceed 20 environmental samples.
	The method blank is prepared from a clean matrix similar to that of the associated samples that is free from target analytes (e.g., Reagent water, Ottawa sand, glass beads, etc.) and is processed along with and under the same conditions as the associated samples. The method blank goes through all of the steps of the process (including as necessary: filtration, clean-ups, etc.).
	Reanalyze or qualify associated sample results when the concentration of a targeted analyte in the blank is at or above the reporting limit as established by the method or by regulation, AND is greater than 1/10 of the amount measured in the sample.
Calibration Blanks	are prepared and analyzed along with calibration standards where applicable. They are prepared using the same reagents that are used to prepare the standards. In some analyses the calibration blank may be included in the calibration curve.
Instrument Blanks	are blank reagents or reagent water that may be processed during an analytical sequence in order to assess contamination in the analytical system. In general, instrument blanks are used to differentiate between contamination caused by the analytical system and that caused by the sample handling or sample prep process. Instrument blanks may also be inserted throughout the analytical sequence to minimize the effect of carryover from samples with high analyte content.
Trip Blank [1]	are required to be submitted by the client with each shipment of samples requiring aqueous and solid volatiles analyses (or as specified in the client's project plan). Additionally, trip blanks may be prepared and analyzed for volatile analysis of air samples, when required by the client. A trip blank may be purchased (certified clean) or is prepared by the laboratory by filling a clean container with pure deionized water that has been purged to remove any volatile compounds. Appropriate preservatives are also added to the container. The trip blank is sent with the bottle order and is intended to reflect the environment that the containers are subjected to throughout shipping and handling and help identify possible sources if contamination is found. The field sampler returns the trip blank in the cooler with the field samples.
Field Blanks [1]	are sometimes used for specific projects by the field samplers. A field blank prepared in the field by filling a clean container with pure reagent water and appropriate preservative, if any, for the specific sampling activity being undertaken. (EPA OSWER)
Equipment Blanks [1]	are also sometimes created in the field for specific projects. An equipment blank is a sample of analyte-free media which has been used to rinse common sampling equipment to check effectiveness of decontamination procedures. (TNI)
Holding Blanks	also referred to as refrigerator or freezer blanks, are used to monitor the sample storage units for volatile organic compounds during the storage of VOA samples in the laboratory

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[1] When known, these field QC samples should not be selected for matrix QC as it does not provide information on the behavior of the target compounds in the field samples. Usually, the client sample ID will provide information to identify the field blanks with labels such as "FB", "EB", or "TB."

Evaluation criteria and corrective action for these controls are defined in the specific standard operating procedure for each analysis.

22.4) Positive Controls

Control samples (e.g., QC indicators) are analyzed with each batch of samples to evaluate data based upon (1) Method Performance (Laboratory Control Sample (LCS) or Blank Spike (BS)), which entails both the preparation and measurement steps; and (2) Matrix Effects (Matrix Spike (MS) (Matrix spikes are not applicable to air) or Sample Duplicate (MD, DUP), which evaluates field sampling accuracy, precision, representativeness, interferences, and the effect of the matrix on the method performed. Each regulatory program and each method within those programs specify the control samples that are prepared and/or analyzed with a specific batch

Note that frequency of control samples vary with specific regulatory, methodology and project specific criteria. Complete details on method control samples are as listed in each analytical SOP.

22.4.1) Method Performance Control - Laboratory Control Sample (LCS)

The LCS measures the accuracy of the method in a blank matrix and assesses method performance independent of potential field sample matrix affects in a laboratory batch.

The LCS is prepared from a clean matrix similar to that of the associated samples that is free from target analytes (for example: Reagent water, Ottawa sand, glass beads, etc.) and is processed along with and under the same conditions as the associated samples. The LCS is spiked with verified known amounts of analytes or is made of a material containing known and verified amounts of analytes, taken through all preparation and analysis steps along with the field samples. Where there is no preparation taken for an analysis (such as in aqueous volatiles), or when all samples and standards undergo the same preparation and analysis process, a calibration verification standard is reported as the LCS. In some instances where there is no practical clean solid matrix available, aqueous LCS's may be processed for solid matrices; final results may be calculated as mg/kg or ug/kg, assuming 100% solids and a weight equivalent to the aliquot used for the corresponding field samples, to facilitate comparison with the field samples.

Certified pre-made reference material purchased from a NIST/A2LA accredited vendor may also be used for the LCS when the material represents the sample matrix or the analyte is not easily spiked (e.g. solid matrix LCS for metals, etc.).

The specific frequency of use for LCS during the analytical sequence is defined in the specific standard operating procedure for each analysis. It is generally 1 for each batch of samples; not to exceed 20 environmental samples.

If the mandated or requested test method, or project requirements, do not specify the spiking components, the laboratory shall spike all reportable components to be reported in the Laboratory Control Sample (and Matrix Spike) where applicable (e.g. no spike of pH). However, in cases where the components interfere with accurate assessment (such as simultaneously spiking chlordane, Toxaphene and PCBs in Method 608), the test method has an extremely long list of components or components are incompatible, at a minimum, a representative number of the listed components (see below) shall be used to control the test method. The selected components of each spiking mix shall represent all chemistries, elution patterns and masses, permit specified analytes and other client requested components. However, the laboratory shall ensure that all reported components are used in the spike mixture within a two-year time period.

- For methods that have 1-10 target analytes, spike all components.
- For methods that include 11-20 target analytes, spike at least 10 or 80%, whichever is greater.
- For methods with more than 20 target analytes, spike at least 16 components.
- Exception: Due to analyte incompatibility in pesticides, Toxaphene and Chlordane are only spiked at client request based on specific project needs.
- Exception: Due to analyte incompatibility between the various PCB aroclors, aroclors 1016 and 1260 are used for spiking as they cover the range of all of the aroclors. Specific aroclors may be used by request on a project specific basis.

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22.5) Sample Matrix Controls

22.5) Table 22-3. Sample Matrix Control

Control Type	Details	
Matrix Spikes (MS)	Use	used to assess the effect sample matrix of the spiked sample has on the precision and accuracy of the results generated by the method used;
	Typical Frequency [1]	At a minimum, with each matrix-specific batch of samples processed, an MS is carried through the complete analytical procedure. Unless specified by the client, samples used for spiking are randomly selected and rotated between different client projects. If the mandated or requested test method does not specify the spiking components, the laboratory shall spike all reportable components to be reported in the Laboratory Control Sample and Matrix Spike. Refer to the method SOP for complete details
	Description	essentially a sample fortified with a known amount of the test analyte(s).
Surrogate	Use	Measures method performance to sample matrix (organics only).
	Typical Frequency [1]	Are added to all samples, standards, and blanks, for all organic chromatography methods except when the matrix precludes its use or when a surrogate is not available. The recovery of the surrogates is compared to the acceptance limits for the specific method. Poor surrogate recovery may indicate a problem with sample composition and shall be reported, with data qualifiers, to the client whose sample produced poor recovery.
	Description	Are similar to matrix spikes except the analytes are compounds with properties that mimic the analyte of interest and are unlikely to be found in environment samples.
Duplicates[2]	Use	For a measure of analytical precision, with each matrix-specific batch of samples processed, a matrix duplicate (MD or DUP) sample, matrix spike duplicate (MSD)**,** or LCS duplicate (LCSD) is carried through the complete analytical procedure.
	Typical Frequency [1]	Duplicate samples are usually analyzed with methods that do not require matrix spike analysis.
	Description	Performed by analyzing two aliquots of the same field sample independently or an additional LCS.
Internal Standards	Use	Are spiked into all environmental and quality control samples (including the initial calibration standards) to monitor the qualitative aspect of organic and some inorganic analytical measurements.
	Typical Frequency [1]	All organic and ICP methods as required by the analytical method.
	Description	Used to correct for matrix effects and to help troubleshoot variability in analytical response and are assessed after data acquisition. Possible sources of poor internal standard response are sample matrix, poor analytical technique or instrument performance.

[1] See the specific analytical SOP for type and frequency of sample matrix control samples.

[2] LCSD's are normally not performed except when regulatory agencies or client specifications require them. The recoveries for the spiked duplicate samples must meet the same laboratory established recovery limits as the accuracy QC samples. If an LCSD is analyzed both the LCS and LCSD must meet the same recovery criteria and be included in the final report. The precision measurement is reported as "Relative Percent Difference" (RPD). Poor precision between duplicates (except LCS/LCSD) may indicate non-homogeneous matrix or sampling.

22.6) Acceptance Criteria (Control Limits)

As mandated by the test method and regulation, each individual analyte in the LCS, MS, or Surrogate Spike is evaluated against the control limits published in the test method. Where there

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are no established acceptance criteria, the laboratory calculates in-house control limits with the use of control charts or, in some cases, utilizes client project specific control limits. When this occurs, the regulatory or project limits will supersede the laboratory's in-house limits.

Note: For methods, analytes and matrices with very limited data (e.g., unusual matrices not analyzed often), interim limits are established using available data or by analogy to similar methods or matrices.

Once control limits have been established, they are verified, reviewed, and updated if necessary on an annual basis unless the method requires more frequent updating. Control limits are established per method (as opposed to per instrument) regardless of the number of instruments utilized.

Laboratory generated % Recovery acceptance (control) limits are generally established by taking + 3 Standard Deviations (99% confidence level) from the average recovery of a minimum of 20-30 data points (more points are preferred).

- Regardless of the calculated limit, the limit should be no tighter than the Calibration Verification (ICV/CCV). (Unless the analytical method specifies a tighter limit).
- In-house limits cannot be any wider than those mandated in a regulated analytical method. Client or contract required control limits are evaluated against the laboratory's statistically derived control limits to determine if the data quality objectives (DQOs) can be achieved. If laboratory control limits are not consistent with DQOs, then alternatives must be considered, such as method improvements or use of an alternate analytical method.
- The lowest acceptable recovery limit will be 10% (the analyte must be detectable and identifiable). Exception: The lowest acceptable recovery limit for Benzidine will be 5% and the analyte must be detectable and identifiable.
- The maximum acceptable recovery limit will be 180%.
- The maximum acceptable RPD limit will be 35% for waters and 50% for soils. The minimum RPD limit is 10%.
- If either the high or low end of the control limit changes by < 5% from previous, the control chart is visually inspected and, using professional judgment, they may be left unchanged if there is no affect on laboratory ability to meet the existing limits.

22.6.1 The lab must be able to generate a current listing of their control limits and track when the updates are performed. In addition, the laboratory must be able to recreate historical control limits. See SOP *EFGS-Q-QD-SOP2819*, Control Charting and Measurement Uncertainties, for more information.

22.6.2 A LCS that is within the acceptance criteria establishes that the analytical system is in control and is used to validate the process. Samples that are analyzed with an LCS with recoveries outside of the acceptance limits may be determined as out of control and should be reanalyzed if possible. If reanalysis is not possible, then the results for all affected analytes for samples within the same batch must be qualified when reported. The internal corrective action process (see Section 10) is also initiated if an LCS exceeds the acceptance limits. Sample results may be qualified and reported without reanalysis if:

- The analyte results are below the reporting limit and the LCS is above the upper control limit.
- If the analytical results are above the relevant regulatory limit and the LCS is below the lower control limit.

Or, for TNI and DoD/DOE work, there are an allowable number of Marginal Exceedances (ME):

<11 analytes	0 marginal exceedances are allowed.
11 – 30 Analytes	1 marginal exceedance is allowed
31-50 Analytes	2 marginal exceedances are allowed
51-70 Analytes	3 marginal exceedances are allowed
71-90 Analytes	4 marginal exceedances are allowed
> 90 Analytes	5 marginal exceedances are allowed

- Marginal exceedances are recovery exceedances between 3 SD and 4 SD from the mean recovery limit (TNI).
- Marginal exceedances must be random. If the same analyte exceeds the LCS control limit repeatedly, it is an indication of a systematic problem. The source of the error must be located

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and corrective action taken. The laboratory has a system to monitor marginal exceedances to ensure that they are random.

Though marginal exceedences may be allowed, the data must still be qualified to indicate it is outside of the normal limits.

22.6.3 If the MS/MSDs do not meet acceptance limits, the MS/MSD and the associated spiked sample is reported with a qualifier for those analytes that do not meet limits. If obvious preparation errors are suspected, or if requested by the client, unacceptable MS/MSDs are reprocessed and reanalyzed to prove matrix interference. A more detailed discussion of acceptance criteria and corrective action can be found in the lab's method SOPs and in Section 10.

22.6.4 If a surrogate standard falls outside the acceptance limits, and if there is not obvious chromatographic matrix interference, reanalyze the sample to confirm a possible matrix effect. If the recoveries confirm or there was obvious chromatographic interference, results are reported from the original analysis and a qualifier is added. If the reanalysis meets surrogate recovery criteria, the second run is reported (or both are reported if requested by the client). Under certain circumstances, where all of the samples are from the same location and share similar chromatography, the reanalysis may be performed on a single sample rather than all of the samples and if the surrogate meets the recovery criteria in the reanalysis, all of the affected samples would require reanalysis.

22.7) Additional Procedures to Assure Quality Control

The laboratory has written and approved method SOPs to assure the accuracy of the test method including calibration (see Section 20), use of certified reference materials (see Section 19) and use of PT samples (see Section 15).

A discussion regarding MDLs, Limit of Detection (LOD) and Limit of Quantitation (LOQ) can be found in Section 17.

- Use of formulae to reduce data is discussed in the method SOPs and in Section 18.
- Selection of appropriate reagents and standards is included in Section 9 and 19.
- A discussion on selectivity of the test is included in Section 5.
- Constant and consistent test conditions are discussed in Section 4.
- The laboratories sample acceptance policy is included in Section 21.

23) REPORTING RESULTS

23.1) Overview

The results of each test are reported accurately, clearly, unambiguously, and objectively in accordance with State and Federal regulations as well as client requirements. Analytical results are issued in a format that is intended to satisfy customer and laboratory accreditation requirements as well as provide the end user with the information needed to properly evaluate the results. Where there is conflict between client requests and laboratory ethics or regulatory requirements, the laboratory's ethical and legal requirements are paramount, and the laboratory will work with the client during project set up to develop an acceptable solution. Refer to Section 7.

A variety of report formats are available to meet specific needs.

In cases where a client asks for simplified reports, there must be a written request from the client. There still must be enough information that would show any analyses that were out of conformance (QC out of limits) and there should be a reference to a full report that is made available to the client. Review of reported data is included in Section 17.

23.2) Test Reports

Analytical results are reported in a format that is satisfactory to the client and meets all requirements of applicable accrediting authorities and agencies. A variety of report formats are available to meet specific needs. The report is printed on laboratory letterhead, reviewed, and signed by the appropriate project manager. At a minimum, the standard laboratory report shall contain the following information:

23.2.1 A report title (e.g., Analytical Report)

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23.2.2 The cover page shall include the laboratory name, address and telephone number.

23.2.3 A unique identification of the report (e.g., Eurofins Seattle Work Order ID/Job #) and on each page an identification in order to ensure the page is recognized as part of the report and a clear identification of the end.

Note: Page numbers of report are represented as page # of ##. Where the first number is the page number and the second is the total number of pages.

23.2.4 A copy of the chain of custody (COC).

- Any COCs involved with Subcontracting are included.

23.2.5 The name and address of client and a project name/number, if applicable.

23.2.6 Client project manager or other contact

23.2.7 Description and unambiguous identification of the tested sample(s) including the client identification code.

23.2.8 Date of receipt of sample, date and time of collection, and date(s) of test preparation and performance, and time of preparation or analysis if the required holding time for either activity is less than or equal to 72 hours.

23.2.9 Date reported or date of revision, if applicable.

23.2.10 Method of analysis including method code (EPA, Standard Methods, etc.).

23.2.11 Reporting limit.

23.2.12 Method detection limits (if requested)

23.2.13 Definition of Data qualifiers and reporting acronyms (e.g. ND).

23.2.14 Sample results.

23.2.15 QC data consisting of method blank, surrogate, LCS, and MS/MSD recoveries and control limits.

23.2.16 Condition of samples at receipt including temperature. This may be accomplished in a narrative or by attaching sample login sheets (Refer to Sec. 23.2.4 – Item 3 regarding additional addenda).

23.2.17 A statement to the effect that the results relate only to the items tested and the sample as received by the laboratory, except when information is provided by the client. When data is provided by the client there shall be a clear identification of it, and a disclaimer shall be put in the report when the client supplied data can affect the validity of the test.

23.2.18 A statement that the report shall not be reproduced except in full, without prior express written approval by the laboratory coordinator.

23.2.19 A signature and title of the person(s) accepting responsibility for the content of the report and date of issue. Authorized signatories are qualified Project Managers appointed by the Manager of Project Managers.

23.2.20 When TNI accreditation is required, the lab shall certify that the test results meet all requirements of TNI or provide reasons and/or justification if they do not.

23.2.21 The laboratory includes a cover letter.

23.2.22 Where applicable, a narrative to the report that explains the issue(s) and corrective action(s) taken in the event that a specific accreditation or certification requirement was not met.

23.2.23 When soil samples are analyzed, a specific identification as to whether soils are reported on a "wet weight" or "dry weight" basis.

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23.2.24 Appropriate laboratory certification number for the state of origin of the sample, if applicable.

23.2.25 If only part of the report is provided to the client (client requests some results before all of it is complete), it must be clearly indicated on the report (e.g., partial report, or how your lab identifies it). A complete report must be sent once all of the work has been completed.

23.2.26 Any non-Eurofins Seattle subcontracted analysis results are provided as a separate report on the official letterhead of the subcontractor. All subcontracting is clearly identified on the report as to which laboratory performed a specific analysis.

23.2.27 A Certification Summary Report, where required, will document that, unless otherwise noted, all analytes tested and reported by the laboratory were covered by the noted certifications.

Note: Refer to the NDSC Document No. CA-I-P-002, Electronic Reporting and Signature Policy, for details on internally applying electronic signatures of approval.

23.2.28 Where the laboratory is responsible for the sampling stage, in addition to the requirements listed above, reports containing the results of sampling shall include the following, where necessary for the interpretation of test results:

- the date of sampling;
- unambiguous identification of the material sampled;
- the location of sampling plan and procedures, and deviations, addition to or exclusions from the sample procedures;
- a reference to the sampling plan and procedure, and deviations, additions to or exclusions from the sample procedures;
- details of any environmental conditions during sampling that affect the interpretation of test results;
- information required to evaluate measurement uncertainty for subsequent testing

23.3) Reporting Level or Report Type

The laboratory offers four levels of quality control reporting. Each level, in addition to its own specific requirements, contains all the information provided in the preceding level. The packages provide the following information in addition to the information described above:

- Level 1 is a report with all of the elements outlined in Section 23.2 above, excluding 23.2.15 (QC data).
- Level II is a Level I report plus summary information, including results for the method blank reported to the laboratory MDL, percent recovery for laboratory control samples and matrix spike samples, and the RPD values for all MSD and sample duplicate analyses.
- Level III contains all the information supplied in Level II, but presented on the CLP-like summary forms, and relevant calibration information. A Level II report is not included, unless specifically requested. No raw data is provided.
- Level IV is the same as Level III with the addition of all raw supporting data.

In addition to the various levels of QC packaging, the laboratory also provides reports in EDD (see below). Initial reports may be provided to clients by facsimile. Procedures used to ensure client confidentiality are outlined in Section 23.6.

23.4) Electronic Data Deliverables (EDDs)

EDDs are routinely offered as part of Eurofins Seattle's services in addition to the test report as described in Section 23.2. When NELAP accreditation is required and both a test report and EDD are provided to the client, the official version of the test report will be the combined information of the report and the EDD. Eurofins Seattle offers a variety of EDD formats including Environmental Restoration Information Management System (ERPIMS), Staged Electronic Data Deliverable (SEDD) Environmental Quality Information System (EQuIS), Electronic Deliverable Format (EDF), Excel and custom files.

EDDs shall be subject to a review to ensure their accuracy and completeness. If EDD generation is automated, review may be reduced to periodic screening if the laboratory can demonstrate that it can routinely generate that EDD without errors. Any revisions to the EDD format must be reviewed

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until it is demonstrated that it can routinely be generated without errors. If the EDD can be reproduced accurately and if all subsequent EDDs can be produced error-free, each EDD does not necessarily require a review.

23.5) Supplemental Information for Test

The lab identifies any unacceptable QC analyses or any other unusual circumstances or observations such as environmental conditions and any non-standard conditions that may have affected the quality of a result. This is typically in the form of a footnote or a qualifier and/or a narrative explaining the discrepancy in the front of the report.

Numeric results with values outside of the calibration range, either high or low are qualified as estimated.

Where quality system requirements are not met, a statement of compliance/non-compliance with requirements and/or specifications is required, including identification of test results derived from any sample that did not meet TNI sample acceptance requirements such as improper container, holding time, or temperature.

Where applicable, a statement on the estimated uncertainty of measurements; information on uncertainty is needed when a client's instructions so require.

When, as requested by the client and agreed to by Eurofins Seattle, the report includes a statement of conformity to specification or standard (see Special Services, Section 5.4), the report shall clearly identify:

- to which results the statement applies,
- which specifications, standard or parts thereof are met or not, and
- the decision rule that was applied (unless the decision rule is inherent in the requested specification or standard, taking into account the level of risk (such as false accept and false reject and statistical assumptions) associated with the decision rule.

Opinions and Interpretations - The test report contains objective information, and generally does not contain subjective information such as opinions and interpretations. If such information is required by the client, the Laboratory Director will determine if a response can be prepared. If so, the Laboratory Director will designate the appropriate member of the management team to prepare a response. The response will be fully documented, and reviewed by the Laboratory Director, before release to the client. There may be additional fees charged to the client at this time, as this is a non-routine function of the laboratory.

Note: Review of data deliverable packages for submittal to regulatory authorities requires responses to non-conforming data concerning potential impact on data quality. This necessitates a limited scope of interpretation, and this work is performed by the QA Department. This is the only form of "interpretation" of data that is routinely performed by the laboratory.

When opinions or interpretations are included in the report, the laboratory provides an explanation as to the basis upon which the opinions and interpretations have been made. Opinions and interpretations are clearly noted as such and where applicable, a comment should be added suggesting that the client verify the opinion or interpretation with their regulator.

23.6) Environmental Testing Obtained From Subcontractors

If the laboratory is not able to provide the client the requested analysis, the samples would be subcontracted following the procedures outlined in the NDSC Document No. CW-L-S-004, Subcontracting.

Data reported from analyses performed by a subcontractor laboratory are clearly identified as such on the analytical report provided to the client. Results from a subcontract laboratory outside of Eurofins are reported to the client on the subcontract laboratory's original report stationary and the report includes any accompanying documentation.

23.7) Client Confidentiality

The laboratory will ensure the highest standards of quality and integrity of the data and services provided to our clients

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The laboratory is responsible for maintaining in confidence all client information obtained or created. In situations involving the transmission of environmental test results by telephone, facsimile or other electronic means, client confidentiality must be maintained.

The laboratory will not intentionally divulge to any person (other than the client or any other person designated by the client in writing) any information regarding the services provided by the laboratory or any information disclosed to the laboratory by the client. Furthermore, information known to be potentially endangering to national security or an entity's proprietary rights will not be released.

Information about the client obtained from sources other than the client (e.g., complainant, regulators) shall be confidential between client and the laboratory. The source of this information shall be confidential to the laboratory and shall not be shared with the client, unless agreed by the source.

Note: This shall not apply to the extent that the information is required to be disclosed by the laboratory under the compulsion of legal process. The laboratory will, to the extent feasible, provide reasonable notice to the client before disclosing the information.

Note: Authorized representatives of an accrediting authority are permitted to make copies of any analyses or records relevant to the accreditation process, and copies may be removed from the laboratory for purposes of assessment.

23.7.1 Report deliverable formats are discussed with each new client. If a client requests that reports be e-mailed, the reports are to meet all requirements of this document.

23.8) Format of Reports

The format of reports is designed to accommodate each type of environmental test carried out and to minimize the possibility of misunderstanding or misuse.

23.9) Amendments to Test Reports

Corrections, additions, or deletions to reports are only made when justification arises through supplemental documentation. Justification is documented using the laboratory's corrective action system (refer to Section 10).

The revised report is retained on the Archive data server, as is the original report. The revised report is stored in the Archive data server under the sample number followed by "Revised". There will be a footnote applied to each page that states the report is revised with a brief explanation of reason for the revision.

23.10) Policies on Client Requests for Amendments

23.10.1) Policy on Data Omissions or Reporting Limit Increases

Fundamentally, our policy is simply to not omit previously reported results (including data qualifiers) or to not raise reporting limits and report sample results as ND. This policy has few exceptions. Exceptions are:

- Laboratory error.
- Sample identification is indeterminate (confusion between COC and sample labels).
- An incorrect analysis (not analyte) was requested (e.g., COC lists 8315 but client wanted 8310). A written request for the change is required.
- Incorrect limits reported based on regulatory requirements.
- The requested change has absolutely *no possible* impact on the interpretation of the analytical results and there is *no possibility* of the change being interpreted as misrepresentation by anyone inside or outside of our company.

23.10.2) Multiple Reports

The laboratory does not issue multiple reports for the same work order where there is different information on each report (this does not refer to copies of the same report) unless required to meet

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regulatory needs and approved by QA.

Appendix.1) List of Governing Documents applicable to the QA Manual
(NDSC and Laboratory SOPs and Policies)

NDSC Doc. No.	Title
CA-I-P-002	Electronic Reporting and Signature Policy
CA-L-P-002	Contract Compliance Policy
CA-Q-M-002	Quality Management Plan
CA-Q-S-001	Acid and Solvent Lot Testing and Approval Program
CA-Q-S-002	Manual Integrations
CA-Q-S-006	Detection and Quantitation Limits
CA-Q-S-009	Root Cause Analysis
CW-E-M-001	Environmental Health & Safety Manual
CW-F-P-004	Procurement and Contracts Policy
CW-L-P-001	Records Retention Policy
CW-L-P-004	Ethics Policy
CW-L-S-002	Internal Investigation
CW-Q-S-001	Document Control and Archiving
CW-L-S-004	Subcontracting
CW-Q-S-003	Internal Auditing
CW-Q-S-004	Management Systems Review
CW-Q-S-005	Data Recall Process
CA-C-S-001	Work Sharing Process
CA-T-P-001	Qualified Products
CW-L-WI-001	Records Retention Schedule
CA-Q-QM-001	Policy on Tentatively Identified Compounds
Local Laboratory Document No.	**Title**
EFGS-S-HS-12066	Chemical Hygiene Plan
EFGS-S-HS-SOP2991	Waste Disposal Procedures for Client Sample Waste
EFGS-S-HS-SOP5670	Health and Safety Evaluation and Auditing
EFGS-P-DR-SOP2801	Data Review and Validation and Monthly Logbook Reviews
EFGS-Q-QD-SOP2804	Creation and Control of Standard Operating Procedures
EFGS-P-SP-SOP5147	Subsampling of Solids and Multiphasic Liquids
EFGS-Q-QD-SOP2802	Document Management System
EFGS-Q-QD-SOP2814	Personnel Training and Demonstration of Capability Procedures
EFGS-Q-QD-SOP2819	Control Charting and Measurement Uncertainties
EFGS-Q-QD-SOP2833	Developing Effective Preventive Actions Through Risk Management
EFGS-Q-QD-SOP2835	Incident Reports, Out-of-Specification Reports and Client Complaints
EFGS-Q-QD-SOP2989	Quality Assurance Audit Procedures and Monthly QA Reports
EFGS-Q-QD-SOP2710	Class 1 Weight Calibration, Balance Verification, Calibration & Maintenance
EFGS-Q-QD-SOP2831	Use, Calibration, and Maintenance of Laboratory Thermometers and Refrigerator and Freezer Temperature Monitoring and Maintenance
EFGS-Q-QD-SOP41922	Receipt, Preparation, Storage and Verification of Standards and Reagents and Traceability Protocols
EFGS-P-PM-SOP2815	Contract Review
EFGS-P-PM-SOP40740	Subcontracting Samples
EFGS-S-P-SOP2809	Ordering Laboratory Supplies/Services and Testing Acid and Bottle Lots
EFGS-P-SH-SOP41445	Sample Receipt and Log-in Using TALS LIMS
EFGS-P-SH-SOP2793	Shipping and Receiving of Client Samples Using Element LIMS
EFGS-T-TM-SOP2839	Stock and Prepared Standards for Trace Metals

Appendix.2) List of Laboratory Certifications, Accreditations, Validations

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The laboratory maintains accreditations, certifications, and approvals with numerous state and national entities. Programs vary but may include on-site audits, reciprocal agreements with another entity, performance testing evaluations, review of the QA Manual, Standard Operating Procedures, Method Detection Limits, training records, etc. At the time of this QA Manual revision, the laboratory has accreditation/ certification/licensing with the following organizations:

Primary NELAP accreditation with Oregon Environmental Laboratory Accreditation Program. Secondary NELAP accreditations with the Florida Department of Health, New York Department of Health, State of Louisiana Department of Environmental Quality, and New Jersey Department of Environmental Protection.

State accreditations by the Washington Department of Ecology the State of Arkansas Department of Environmental Quality, State of Alaska Department of Environmental Quality, State of California Water Boards, State of Maine Department of Health, Montana Department of Environmental Quality and Human Services, State of Wisconsin Department of Natural Resources.

ISO/IEC 17025:2017, DoD and DOE accredited

A certification summary with expiration dates and PDF files of current ISO/IEC 17025:2017, NELAP, federal and state accreditations and registrations with their scopes are located at: \\us34fivp002\General and Admin\Quality Assurance\Certifications-Apps-Approval\Current Certs

Appendix.3) References used to prepare the QA Manual

The QAM has been prepared to be consistent with the requirements of the following documents:

- ANSI/ASQC, E4-1994, "Specifications and Guidelines for Quality Management Systems for Environmental Data Collection and Environmental Technology Programs" (American National Standard, January 5, 1995, or most recent version)
- "EPA Requirements for Quality Management Programs" (QA/R-2) (EPA/240/B-01/002, May 31, 2006).
- EPA 600/4-79-019, Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA, March 1979.
- Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996; Final Update IV, January 2008; Final Update V, August 2015.
- U.S. Department of Defense (DoD)/Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories, Version 5.3, dated 2019
- Federal Register, 40 CFR Parts 136, 141, 172, 173, 178, 179 and 261.
- Statement of Work for Inorganics & Organics Analysis, SOM and ISM, current versions, USEPA Contract Laboratory Program Multi-media, Multi-concentration.
- APHA, Standard Methods for the Examination of Water and Wastewater, 18th Edition, 19th, 20th, 21st, 22nd and on-line Editions.
- U.S. Department of Energy Order 414.1B, Quality Assurance, Approved April 29, 2004.
- U.S. Department of Energy Order 414.1C, Quality Assurance, June 17, 2005.
- U.S. Department of Energy Order 414.1D, Quality Assurance, April, 25, 2011.
- Nuclear Regulatory Commission (NRC) Quality Assurance Requirements.
- Marine Protection, Research, and Sanctuaries Act (MPRSA).
- Toxic Substances Control Act (TSCA).

Appendix.4) QA Manual Crosswalk with TNI and ISO/IEC 17025 Standards

Sec. No.	Title	2009 and 2016 TNI Standard Reference	ISO/IEC 17025:2005(E) Reference	ISO/IEC 17025:2017(E) Reference
-	QUALITY ASSURANCE MANUAL	V1M2 Sec. 4.2.8.3		
	Title Page			
	Table of Contents	V1M2 Secs. 4.2.8.3-4.2.8.4		8.1.2, 8.2.1

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Sec. No.	Title	2009 and 2016 TNI Standard Reference	ISO/IEC 17025:2005(E) Reference	ISO/IEC 17025:2017(E) Reference
1.0	Introduction, Scope and Applicability	V1M2 Sec. 4.2.8.4		
1.1	Introduction and Compliance References	V1M2 Secs. 1.1; 1.2; 2.0; 3.2; 4.1.2; 4.2.4	4.1.2; 4.2.4	5.3; 5.4; 8.2.4; 8.3.1
1.2	Terms and Definitions	V1M2 Secs. 3.0; 4.2.4	4.2.4	
1.3	Scope /Field of Testing	V1M2 Secs. 1.2; 4.2.4	4.1.2; 4.2.4	5.3; 5.4; 8.2.1; 8.2.4
1.4	Management of The Manual	V1M2 Secs. 4.2.1; 4.2.7; 4.3.3.2; 4.3.3.3	4.2.1; 4.2.7; 4.3.3.2; 4.3.3.3	5.3
2.0	Management and Responsibilities	V1M2 Sec. 4		8.2.4; 8.2.5
2.1	Overview	V1M2 Secs. 4.1.1, 4.1.3; 4.1.5	4.1.1; 4.1.3; 4.1.5; 4.2.6	5.1; 5.2; 5.5; 5.6; 6.2.1; 6.2.4
2.2	Roles and Responsibilities	V1M2 Secs. 4.1.4; 4.1.5; 4.1.6; 4.2.1; 4.2.6; 5.2.4	4.1.3; 4.1.5; 4.1.6; 4.2.1; 4.2.6; 5.2.4	4.1.1 to 4.1.3; 4.1.5; 5.5; 5.6; 6.2.1; 6.2.4; 6.2.6 8.2.2;
2.3	Business Continuity and Contingency Plan *(Prev. Deputies)*	V1M2 Secs. 4.1.5; 4.1.7.2; 4.2.7	4.1.5; 4.2.7	
3.0	PERSONNEL	V1M2 Secs. 5.2; 5.2.1	5.2.1	6.1; 6.2.3
3.1	Overview	V1M2 Secs. 5.2.2; 5.2.3; 5.2.5	5.2.2; 5.2.3; 5.2.5	6.2.2
3.2	Education and Experience Requirements for Technical Staff	V1M2 Secs. 5.2.1; 5.2.3; 5.2.4	5.2.1; 5.2.3; 5.2.4	6.2.2 to 6.2.4
3.3	Training	V1M2 Sec. 5.2.5	5.2.5	4.2.1; 6.2.2; 6.2.4; 6.2.5
3.4	Data Integrity and Ethics Training Program	V1M2 Sec. 4.2.8.1; 5.2.7		4.1.1
4.0	ACCOMMODATIONS AND ENVIRONMENTAL CONDITIONS	V1M2 Sec. 5.3		6.1; 6.3.1
4.1	Overview	V1M2 Secs. 5.3.1; 5.3.3; 5.3.4; 5.3.5	5.3.1; 5.3.3; 5.3.4; 5.3.5	6.3.1
4.2	Environment	V1M2 Secs. 5.3.1; 5.3.2; 5.3.3; 5.3.4; 5.3.5	5.3.1; 5.3.2; 5.3.3; 5.3.4; 5.3.5	6.3.1 to 6.3.5
4.3	Work Area	V1M2 Secs. 5.3.3; 5.3.4; 5.3.5	5.3.3; 5.3.4; 5.3.5	6.3.1
4.4	Responding to Emergencies			
4.5	Building Security	V1M2 Sec. 5.3.4	5.3.4	6.3.4
5.0	QUALITY SYSTEM			6.1; 8.2.4
5.1	Quality Policy	V1M2 Secs. 4.1.5; 4.2.2; 4.2.3; 4.2.8.3	4.1.5; 4.2.2; 4.2.3	8.2.3; 8.6.1

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Sec. No.	Title	2009 and 2016 TNI Standard Reference	ISO/IEC 17025:2005(E) Reference	ISO/IEC 17025:2017(E) Reference
5.2	Ethics and Data Integrity	V1M2 Secs. 4.1.5; 4.16; 4.2.2; 4.2.8.1; 5.2.7	4.1.5; 4.2.2	4.1.1 to 4.1.3; 4.2.1; 6.2.1; 8.2.2; 8.2.3
5.3	Quality System Documentation	V1M2 Secs. 4.1.5; 4.2.2; 4.2.5	4.2.2; 4.2.5	8.2.4
5.4	QA/QC Objectives for the Measurement of Data	V1M2 Sec. 4.2.2	4.1.5; 4.2.2	6.2.4
5.5	Criteria for Quality Indicators			
5.6	Statistical Quality Control			
5.7	Quality System Metrics			
6.0	Document Control	V1M2 Secs. 4.2.7; 4.3.1; 4.3.2.2 ; 4.3.3.3; 4.3.3.4	4.2.7; 4.3.1; 4.3.2.2; 4.3.3.3; 4.3.3.4	8.2.4; 8.3.1
6.1	Overview			8.2.5; 8.3.1; 8.3.2
6.2	Document Approval and Issue	V1M2 Secs. 4.3.2; 4.3.2.1-4.3.2.3; 4.3.3.1	4.3.2.1; 4.3.2.2; 4.3.2.3; 4.3.3.1	8.2.5; 8.3.2
6.3	Procedures for Document Control Policy	V1M2 Secs. 4.3.2.1–4.3.2.2; 4.3.3.1	4.3.2.1; 4.3.2.2; 4.3.3.1	8.2.5; 8.3.2
6.4	Obsolete Documents	V1M2 Secs. 4.3.2.1–4.3.2.2	4.3.2.1; 4.3.2.2	8.2.5; 8.3.2
7.0	SERVICE TO THE CLIENT	V1M2 Secs. 4.4.1 - 4.4.4	4.4.1; 4.4.2; 4.4.3; 4.4.4	7.1.1; 7.1.1.4; 7.1.1.5; 7.1.1.8; 7.1.2.1
7.1	Overview	V1M2 Secs. 4.4.5; 4.5.5; 5.7.1	4.4.5; 5.7.1	
7.2	Review Sequence and Key Personnel	V1M2 Sec. 4.4.5	4.4.5	7.1.1.6
7.3	Balancing Laboratory Work Load and Capacity			
7.4	Documentation	V1M2 Sec. 5.7.1	5.7.1	
7.5	Special Services	V1M2 Secs. 4.7.1-4.7.2	4.7.1; 4.7.2	7.1.1.3; 7.1.1.7
7.6	Client Communication	V1M2 Secs. 4.7.1-4.7.2	4.7.1; 4.7.2	7.1.1.7
7.7	Reporting	V1M2 Secs. 4.7.1-4.7.2	4.7.1; 4.7.2	7.1.1.7
7.8	Client Feedback and Surveys	V1M2 Secs. 4.7.1-4.7.2	4.7.1; 4.7.2	7.1.1.7; 8.6.2
8.0	SUBCONTRACTING OF TESTS	V1M2 Secs. 4.4.3; 4.5.4	4.4.3; 4.5.4	
8.1	Overview	V1M2 Secs. 4.5.1 - 4.5.3; 4.5.5; 5.3.1	4.5.1; 4.5.2; 4.5.3; 5.3.1	6.6.1; 7.1.2.1; 7.1.2.2
8.2	Qualifying and Monitoring Subcontractors	V1M2 Secs. 4.5.1; 4.5.2; 4.5.3; 4.5.5	4.5.1; 4.5.2; 4.5.3	6.6.1; 7.1.2.1; 7.1.2.2
8.3	Oversight and Reporting	V1M2 Sec. 4.5.5		
8.4	Contingency Planning			

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Sec. No.	Title	2009 and 2016 TNI Standard Reference	ISO/IEC 17025:2005(E) Reference	ISO/IEC 17025:2017(E) Reference
8.5	Use of NELAP and A2LA Logo			
9.0	PURCHASING SERVICES AND SUPPLIES	V1M2 Sec. 4.6.1	4.6.1	
9.1	Overview	V1M2 Secs. 4.6.2; 4.6.3; 4.6.4	4.6.2; 4.6.3; 4.6.4	6.6.1; 6.6.2
9.2	Glassware	V1M2 Sec. 5.5.13.1		
9.3	Reagents, Standards & Supplies	V1M2 Secs. 4.6.2; 4.6.3; 4.6.4 2016 V1M4 1.7.2.5	4.6.2; 4.6.3; 4.6.4	6.6.1 to 6.6.3
9.4	Purchase of Equipment / Instruments / Software			
9.5	Services			
9.6	Suppliers			
10.0	COMPLAINTS	V1M2 Sec. 4.8	4.8	8.6.1; 8.6.2
10.1	Overview			7.9.1 to 7.9.3 8.6.1; 8.6.2;
10.2	External Complaints			7.9.2 to 7.9.7 8.6.1; 8.6.2;
10.3	Internal Complaints			8.6.1; 8.6.2
10.4	Management Review			8.6.1; 8.6.2
11.0	CONTROL OF NON-CONFORMING WORK	V1M2 Secs. 4.9.1; 5.10.5	4.9.1; 5.10.5	7.10.1
11.1	Overview	V1M2 Secs. 4.9.1; 4.11.3; 4.11.5	4.9.1; 4.11.3; 4.11.5	7.10.1
11.2	Responsibilities and Authorities	V1M2 Secs. 4.9.1; 4.11.3; 4.11.5; 5.2.7	4.9.1; 4.11.3; 4.11.5	7.10.1
11.3	Evaluation of Significance and Action Taken	V1M2 Secs. 4.9.1; 4.11.3; 4.11.5	4.9.1; 4.11.3; 4.11.5	4.1.5; 7.10.1; 7.10.2; 8.5.3
11.4	Prevention of Non-Conforming Work	V1M2 Secs. 4.9.4; 4.11.2	4.9.2; 4.11.2	7.10.2; 7.10.3; 8.5.3
11.5	Method Suspension / Restriction (Stop Work Procedures)	V1M2 Secs. 4.9.1; 4.9.2; 4.11.5	4.9.1; 4.9.2; 4.11.5	7.10.1; 7.10.2
12.0	CORRECTIVE ACTION	V1M2 Sec. 4.11		4.1.4; 4.1.5
12.1	Overview	V1M2 Secs. 4.9.2; 4.11.1; 4.11.2	4.9.2; 4.11.1; 4.11.2; 8.7.1; 8.7.3	7.10.2 8.7.1; 8.7.3;
12.2	General	V1M2 Sec. 4.11.2; 4.11.3	4.11.2; 4.11.3	7.7.2; 8.5.3; 8.7.1;
12.3	Closed Loop Correction Action Process	V1M2 Sec. 4.11.2; 4.11.3; 4.11.4; 4.11.6; 4.11.7; 4.12.2	4.11.2; 4.11.3; 4.11.4; 4.12.2	8.5.3; 8.6.1; 8.7.2
12.4	Technical Corrective Actions	V1M2 Sec. 4.11.6		8.7.1

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Sec. No.	Title	2009 and 2016 TNI Standard Reference	ISO/IEC 17025:2005(E) Reference	ISO/IEC 17025:2017(E) Reference
12.5	Basic Corrections	V1M2 Secs. 4.11.1; 4.13.2.3	4.11.1; 4.13.2.3	7.5.2; 8.7.1
13.0	PREVENTIVE ACTION / IMPROVEMENT	V1M2 Secs. 4.10; 4.12.1; 4.12.2	4.10; 4.12.1; 4.12.2	4.1.4
13.1	Overview	V1M2 Secs. 4.15.1; 4.15.2	4.15.1; 4.15.2	8.6.2
13.2	Management of Change			
14.0	CONTROL OF RECORDS	V1M2 Secs. 4.2.7; 4.13.1.1; 4.13.3	4.2.7; 4.13.1.1	8.4.2
14.1	Overview	V1M2 Secs. 4.13.1.1 - 4.13.1.4; 4.13.2.1- 4.13.2.3; 4.13.3	4.13.1.1 - 4.13.1.4; 4.13.2.1- 4.13.2.3	8.4.1; 8.4.2
14.2	Programs with Longer Retention Requirements			
14.3	Technical and Analytical Records	V1M2 Sec. 4.13.2.2 - 4.13.2.3	4.13.2.2; 4.13.2.3	7.5.1; 8.4.2
14.4	Laboratory Support Activities			7.5.2; 8.4.2
14.5	Administrative Records			8.4.2
14.6	Records Management, Storage and Disposal	V1M2 Sec. 4.13.3		4.2.1; 8.4.2
15.0	AUDITS			
15.1	Internal Audits	V1M2 Sec. 4.2.8.1; 4.14; 4.14.1; 4.14.2 ; 4.14.3; 4.14.5; 5.9.1; 5.9.2	4.14.1; 4.14.2; 4.14.3; 5.9.1; 5.9.2	8.6.1; 8.8.1; 8.8.2
15.2	External Audits	V1M2 Secs.4.14.2; 4.14.3	4.14.2; 4.14.3; 4.14.4	4.2.1; 8.6.1
15.3	Audit Findings	V1M2 Secs. 4.14.2; 4.14.3; 4.14.5		8.6.1
16.0	MANAGEMENT REVIEWS	V1M2 Sec. 4.1.6; 4.15; 4.15.1; 4.15.2	4.1.6; 4.15.1; 4.15.2	4.1.4; 8.5.1; 8.6.1; 8.9.1; 8.9.2
16.1	Quality Assurance Report			8.5.1
16.2	Annual Management Review	V1M2 Sec. 4.2.2; 4.15.3	4.2.2	4.1.1, 4.1.4; 4.2.1; 7.1.1.3; 8.2.2; 8.5.1 to 8.5.3; 8.6.1; 8.9.3
16.3	Potential Integrity Related Managerial Reviews			4.1.5; 8.5.1; 8.6.1
17.0	TEST METHODS AND METHOD VALIDATION	V1M2 Sec. 5.4.1	5.4.1	7.2.1.1; 8.2.5
17.1	Overview	V1M2 Sec. 5.4.1	5.4.1; 5.4.5.1	6.2.3; 7.2.1.1 to 7.2.1.3

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Sec. No.	Title	2009 and 2016 TNI Standard Reference	ISO/IEC 17025:2005(E) Reference	ISO/IEC 17025:2017(E) Reference
17.2	Standard Operating Procedures (SOPs)	V1M2 Secs. 4.2.8.5; 4.3.3.1; 5.4.2	4.3.3.1; 5.4.2	7.2.1.4
17.3	Laboratory Methods Manual	V1M2 Sec. 4.2.8.5 (2019 5.4.4.2)		6.2.3
17.4	Selection of Methods	V1M2 Secs. 4.13.3; 5.4.1; 5.4.2; 5.4.3. (2019 5.4.4) V1M4 Secs. 1.4; 1.5.1; 1.6.1; 1.6.2; 1.6.2.1; 1.6.2.2	5.4.1; 5.4.2; 5.4.3; 5.4.4; 5.4.5.1; 5.4.5.2; 5.4.5.3	7.1.1.2; 7.2; 7.2.1.2; 7.2.1.3; 7.1.2.4 to 7.2.1.7; 7.2.2.1 to 7.2.1.7; 7.2.2.1
17.5	Laboratory Developed Methods and and Non-Standard Methods	V1M2 Sec. 5.4.2. (2019 5.4.4.1, 5.4.4.2) V1M4 Sec. 1.5.1	5.4.2; 5.4.4; 5.4.5.2; 5.4.5.3	7.1.1.2; 7.2.1.4 to 7.2.1.7 7.2.2.1; 7.2.2.3; 8.2.5
17.6	Validation of Methods	V1M2 Sec. 5.4.2. (2019 5.4.5.4) V1M4 Secs. 1.5.1; 1.5.2; 1.5.2.1; 1.5.2.2; 1.5.3	5.4.2; 5.4.4; 5.4.5.2; 5.4.5.3	7.1.1.2; 7.1.2.4; 7.2.1.6; 7.2.2.1 to 7.2.2.4
17.7	Method Detection Limits (MDLs) / Limit of Detection (LOD)	V1M2 Sec. 5.9.3. V1M4 Secs. 1.5.2; 1.5.2.1; 1.5.2.2	5.4.5.3	7.2.2.3
17.8	Verification of Detection Limits	V1M2 Sec. 5.9.3		
17.9	Instrument Detection Limits (IDLs)	V1M2 Sec. 5.9.3. V1M4 Sec. 1.5.2.1		
17.10	Limit of Quantitation	V1M2 Sec. 5.9.3		
17.11	Retention Windows	V1M2 Sec. 5.9.3. V1M4 Sec. 1.5.4; (2009 1.7.3.6) (2016 1.7.2.6)		
17.12	Evaluation of Selectivity	V1M2 Sec. 5.9.3. V1M4 Sec. 1.5.4; (2009 1.7.3.6) (2016 1.7.2.6)		
17.13	Estimation of Uncertainty of Measurement	V1M2 Sec. 5.1.1; 5.1.2; 5.4.6	5.1.1; 5.1.2; 5.4.6.1; 5.4.6.2; 5.4.6.3	7.6.1; 7.6.2; 7.6.3
17.14	Sample Reanalysis Guidelines	V1M2 Sec 5.9.1	5.9.1	
17.15	Control of Data	V1M2 Secs. 5.4.7.1; 5.4.7.2; 5.9.1	5.4.7.1; 5.4.7.2; 5.9.1	7.11.1 to 7.11.6
18.0	EQUIPMENT AND CALIBRATIONS	V1M2 Secs. 5.5.4; 5.5.5; 5.5.6	5.5.4; 5.5.5; 5.5.6; 5.6.1	6.1; 6.4.3; 6.4.6; 6.4.9
18.1	Overview	V1M2 Secs. 5.5.1; 5.5.2; 5.5.3; 5.5.5; 5.5.10	5.5.1; 5.5.2; 5.5.3; 5.5.5; 5.5.10; 5.6.1	6.4.1; 6.4.4 to 6.4.6; 6.4.9; 6.4.11

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Sec. No.	Title	2009 and 2016 TNI Standard Reference	ISO/IEC 17025:2005(E) Reference	ISO/IEC 17025:2017(E) Reference
18.2	Preventive Maintenance	V1M2 Secs. 5.5.1; 5.5.3; 5.5.7; 5.5.9	5.5.1; 5.5.3; 5.5.7; 5.5.9; 5.6.1	6.4.1 to 6.4.3; 6.4.6; 6.4.10
18.3	Support Equipment	V1M2 Secs. 5.5.10; 5.5.11; 5.5.13.1	5.5.10; 5.5.11; 5.6.2.1.2; 5.6.2.2.1; 5.6.2.2.2	6.4.11; 6.4.12; 6.5.1; 6.5.2; 6.5.3
18.4	Instrument Calibrations	V1M2 Secs. 5.5.8; 5.5.10; 5.6.3.1. V1M4 Sec. 1.7.1.1; (2009 1.7.2) (2016 1.7.1.2)	5.5.8; 5.5.9; 5.5.10; 5.6.1; 5.6.2; 5.6.3.1	6.4.2; 6.4.3; 6.4.6 to 6.4.8; 6.4.11; 6.4.13; 6.4.14; 6.5.1; 6.5.2
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18.6	GC/MS Tuning			
19.0	MEASUREMENT OF TRACEABILITY			
19.1	Overview	V1M2 Sec. 5.6.3.1	5.6.2.1.2; 5.6.2.2.2; 5.6.3.1	6.4.14; 6.5.1; 6.5.2; 6.5.3
19.2	NIST-Traceable Weights and Thermometers	V1M2 Secs. 5.5.13.1; 5.6.3.1; 5.6.3.2	5.6.3.1; 5.6.3.2	6.4.14
19.3	Reference Standards / Materials	V1M2 Secs. 5.6.3.1; 5.6.3.2; 5.6.3.3; 5.6.3.4; 5.6.4.1; 5.6.4.2; 5.9.1; 5.9.3	5.6.3.1; 5.6.3.2; 5.6.3.3; 5.6.3.4; 5.9.1	6.4.14
19.4	Documentation and Labeling of Standards, Reagents, and Reference Materials	V1M2 Secs. 5.6.4.2; 5.9.3		
20.0	SAMPLING			
20.1	Overview	V1M2 Secs. 5.7.1; 5.7.3	5.7.1; 5.7.3	7.3.1; 7.3.2; 7.3.3
20.2	Sampling Containers			
20.3	Definition of Holding Time			
20.4	Sampling Containers, Preservation Requirements, Holding Times			
20.5	Sample Aliquots / Subsampling	V1M2 Sec. 5.7.1	5.7.1	7.3.1; 7.3.2
21.0	HANDLING OF SAMPLES	V1M2 Sec. 5.8.1	5.8.1	7.4.1
21.1	Chain of Custody (CoC)	V1M2 Secs. 5.7.2; 5.7.4; 5.8.4; 5.8.7.5; 5.8.8; 5.9.1	5.7.2; 5.8.4; 5.9.1	7.1.1.6; 7.4.1
21.2	Sample Receipt	V1M2 Secs. 5.8.1; 5.8.2; 5.8.3; 5.8.5; 5.8.7.3; 5.8.7.4; 5.8.7.5	5.8.2; 5.8.3	7.4.3
21.3	Sample Acceptance Policy	V1M2 Secs. 5.8.6; 5.8.7.2		
21.4	Sample Storage	V1M2 Secs. 5.7.4; 5.8.4	5.8.4	7.4.1; 7.4.4

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22.0	ASSURING THE QUALITY OF TEST RESULTS			
22.1	Overview	V1M2 Secs. 5.9.2; 5.9.3	5.9.2	7.7.2 to 7.7.3
22.2	Controls	V1M2 Secs. 5.9.2; 5.9.3	5.9.2	7.7.1; 7.7.3
22.3	Negative Controls	V1M2 Secs. 5.9.2; 5.9.3 V1M4 Secs. (2019 1.7.3; 1.7.3.1; 1.7.4.1) (2016 1.7.2, 1.7.2.1, 1.7.3.1)	5.9.2	7.7.1; 7.7.3
22.4	Positive Controls	V1M2 Secs 5.9.2; 5.9.3. V1M4 Secs. (2009 1.7.3; 1.7.3.2; 1.7.3.2.1; 1.7.3.2.2; 1.7.3.2.3) (2016 1.7.2, 1.7.2.2, 1.7.3.2)	5.9.2	7.7.1; 7.7.3
22.5	Sample Matrix Controls	V1M2 Secs. 5.9.2; 5.9.3. V1M4 Secs. (2009 1.7.3 ; 1.7.3.3; 1.7.3.3.1; 1.7.3.3.2; 1.7.3.3.3) (2016 1.7.2, 1.7.2.3, 1.7.3.3)	5.9.2	7.7.1; 7.7.3
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22.7	Additional Procedures to Assure Quality Control	V1M2 Sec. 5.9.3. V1M4 Sec. (2009 1.7.3.4), (2016 1.7.2.4)		7.7.1; 7.7.3
23.0	REPORTING RESULTS			
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23.3	Reporting Level or Report Type	V1M2 Secs. 5.10.1; 5.10.7; 5.10.8	5.10.1; 5.10.7; 5.10.8	
23.4	Electronic Data Deliverables (EDDs)			
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Appendix.5) Terms/Glossary and Acronyms (EL-V1M2 Sec. 3.1)
Terms/Glossary:

Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents. (ASQC)
Accreditation: The process by which an agency or organization evaluates and recognizes a laboratory as meeting certain predetermined qualifications or standards, thereby accrediting the laboratory.
Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator. (QAMS)
Analyst: The designated individual who performs the "hands-on" analytical methods and associated techniques and who is the one responsible for applying required laboratory practices and other pertinent quality controls to meet the required level of quality.
Analytical Uncertainty: A subset of Measurement Uncertainty that includes all laboratory activities performed as part of the analysis. (TNI)
Anomaly: A condition or event, other than a deficiency, that may affect the quality of the data, whether in the laboratory's control or not.
Assessment: The evaluation process used to measure or establish the performance, effectiveness, and conformance of an organization and/or its systems to defined criteria (to the standards and requirements of laboratory accreditation). (TNI)
Audit: A systematic and independent examination of facilities, equipment, personnel, training, procedures, record-keeping, data validation, data management, and reporting aspects of a system to determine whether QA/QC and technical activities are being conducted as planned and whether these activities will effectively achieve quality objectives. (TNI)
Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one (1) to twenty (20) environmental samples of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be twenty-four (24) hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples. (TNI)
Bias: The systematic or persistent distortion of a measurement process, which causes errors in one direction (i.e., the expected sample measurement is different from the sample's true value). (TNI)
Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results. (ASQC)
Calibration: A set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material, and the corresponding values realized by standards. (TNI)

1) In calibration of support equipment the values realized by standards are established through the use of reference standards that are traceable to the International System of Units (SI).
2) In calibration according to methods, the values realized by standards are typically established through the use of Reference Materials that are either purchased by the laboratory with a certificate of analysis or purity, or prepared by the laboratory using support equipment that has been calibrated or verified to meet specifications.
Calibration Curve: The mathematical relationship between the known values, such as concentrations, of a series of calibration standards and their instrument response. (TNI)
Calibration Standard: A substance or reference material used to calibrate an instrument (QAMS)
Certified Reference Material (CRM): A reference material accompanied by a certificate, having a value, measurement uncertainty, and stated metrological traceability chain to a national metrology institute. (TNI)
Chain of Custody (COC) Form: Record that documents the possession of the samples from the time of collection to receipt in the laboratory. This record generally includes: the number and types of containers; the mode of collection; the collector; time of collection; preservation; and requested analyses. (TNI)
Compromised Samples: Those samples which are improperly sampled, insufficiently documented (chain of custody and other sample records and/or labels), improperly preserved, collected in improper containers, or exceeding holding times when delivered to a laboratory. Under normal conditions, compromised samples are not analyzed. If emergency situation require analysis, the results must be appropriately qualified.

Confidential Business Information (CBI): Information that an organization designates as having the potential of providing a competitor with inappropriate insight into its management, operation or products. TNI and its representatives agree to safeguard identified CBI and to maintain all information identified as such in full confidentiality.
Confirmation: Verification of the identity of a component through the use of an approach with a different scientific principle from the original method. These may include, but are not limited to Second Column Confirmation; Alternate wavelength; Derivatization; Mass spectral interpretation; Alternative detectors or Additional Cleanup procedures. (TNI)
Conformance: An affirmative indication or judgment that a product or service has met the requirements of the relevant specifications, contract, or regulation; also the state of meeting the requirements. (ANSI/ASQC E4-1994)
Correction: Actions necessary to correct or repair analysis specific non-conformances. The acceptance criteria for method specific QC and protocols as well as the associated corrective actions. The analyst will most frequently be the one to identify the need for this action as a result of calibration checks and QC sample analysis. No significant action is taken to change behavior, process or procedure.
Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence. (ISO 8402)
Data Integrity: The condition that exists when data are sound, correct, and complete, and accurately reflect activities and requirements. (TNI)
Data Audit: A qualitative and quantitative evaluation of the documentation and procedures associated with environmental measurements to verify that the resulting data re of acceptable quality (i.e., that they meet specified acceptance criteria).
Data Reduction: The process of transforming the number of data items by arithmetic or statistical calculations, standard curves, and concentration factors, and collation into a more useable form. (TNI)
Deficiency: An unauthorized deviation from acceptable procedures or practices, or a defect in an item (ASQC), whether in the laboratory's control or not.
Demonstration of Capability: A procedure to establish the ability of the analyst to generate analytical results of acceptable accuracy and precision. (TNI)
Document Control: The act of ensuring that documents (and revisions thereto) are proposed, reviewed for accuracy, approved for release by authorized personnel, distributed properly, and controlled to ensure use of the correct version at the location where the prescribed activity if performed. (ASQC)
Duplicate Analyses: The analyses or measurements of the variable of interest performed identically on two subsamples of the same sample. The results from duplicate analyses are used to evaluate analytical or measurement precision but not the precision of sampling, preservation or storage internal to the laboratory. (EPA-QAD)
Equipment Blank: Sample of analyte-free media which has been used to rinse common sampling equipment to check effectiveness of decontamination procedures.
External Standard Calibration: Calibrations for methods that do not utilize internal standards to compensate for changes in instrument conditions.
Field Blank: Blank prepared in the field by filing a clean container with pure de-ionized water and appropriate preservative, if any, for the specific sampling activity being undertaken (EPA OSWER)
Field of Accreditation: Those matrix, technology/method, and analyte combinations for which the accreditation body offers accreditation.
Holding Times: The maximum time that samples may be held prior to analyses and still be considered valid or not compromised. (40 CFR Part 136)
Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical test method. (TNI)
Internal Standard Calibration: Calibrations for methods that utilize internal standards to compensate for changes in instrument conditions.
Instrument Blank: A clean sample (e.g., distilled water) processed through the instrumental steps of the measurement process; used to determine instrument contamination. (EPA-QAD)
Instrument Detection Limit (IDL): The minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific instrument. The IDL is associated with the instrumental portion of a specific method only, and sample preparation steps are not considered in its derivation. The IDL is a statistical estimation at a specified confidence interval of the concentration at which the relative uncertainty is + 100%. The IDL represents a range where qualitative detection occurs on a specific instrument. Quantitative results are not produced in this range.
Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of

analytes, taken through all preparation and analysis steps of the procedure unless otherwise noted in a reference method. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.
An LCS shall be prepared at a minimum of 1 per batch of 20 or less samples per matrix type per sample extraction or preparation method except for analytes for which spiking solutions are not available such as total suspended solids, total dissolved solids, total volatile solids, total solids, pH, color, odor, temperature, dissolved oxygen or turbidity. The results of these samples shall be used to determine batch acceptance.
Least Squares Regression (1st Order Curve): The least squares regression is a mathematical calculation of a straight line over two axes. The y axis represents the instrument response (or Response ratio) of a standard or sample and the x axis represents the concentration. The regression calculation will generate a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.99 for organics and 0.995 for inorganics.
Limit(s) of Detection (LOD) [a.k.a., Method Detection Limit (MDL)]: The MDL is the minimum measured quantity of a substance that can be reported with 99% confidence that the concentration is distinguishable from method blank results, consistent with 40CFR Part 136 Appendix B, August, 2017.
Limit(s) of Quantitation (LOQ) [a.k.a., Reporting Limit]: The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.
(QS) Matrix: The component or substrate that contains the analyte of interest. For purposes of batch and QC requirement determinations, the following matrix distinctions shall be used:
Aqueous: Any aqueous sample excluded from the definition of Drinking Water or Saline/Estuarine. Includes surface water, groundwater effluents, and TCLP or other extracts.
Drinking Water: Any aqueous sample that has been designated as a potable or potential potable water source.
Saline/Estuarine: Any aqueous sample from an ocean or estuary, or other salt water source such as the Great Salt Lake.
Non-Aqueous Liquid: Any organic liquid with <15% settleable solids.
Biological Tissue: Any sample of a biological origin such as fish tissue, shellfish, or plant material. Such samples shall be grouped according to origin.
Solids: Includes soils, sediments, sludges, and other matrices with >15% settleable solids.
Chemical Waste: A product or by-product of an industrial process that results in a matrix not previously defined.
Air & Emissions: Whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas or vapor that are collected with a sorbant tube, impinger solution, filter, or other device. (TNI)
Matrix Spike (spiked sample or fortified sample): A sample prepared, taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a referenced method, by adding a known amount of target analyte to a specified amount of sample for which an independent test result of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.
Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A replicate matrix spike prepared and analyzed to obtain a measure of the precision of the recovery for each analyte.
Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.
Method Detection Limit: See Limit of Detection (LOD)
Negative Control: Measures taken to ensure that a test, its components, or the environment do not cause undesired effects, or produce incorrect test results.
Non-conformance: An indication, judgment, or state of not having met the requirements of the relevant specifications, contract, or regulation.
Observation: A record of phenomena that (1) may assist in evaluation of the sample data; (2) may be of importance to the project manager and/or the client, and yet not at the time of the observation have any known effect on quality.
Performance Audit: The routine comparison of independently obtained qualitative and quantitative measurement system data with routinely obtained data in order to evaluate the proficiency of an analyst or laboratory.
Positive Control: Measures taken to ensure that a test and/or its components are working properly and producing correct or expected results from positive test subjects.
Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is

usually expressed as standard deviation, variance or range, in either absolute or relative terms. (TNI)

Preservation: Any conditions under which a sample must be kept in order to maintain chemical and/or biological integrity prior to analysis. (TNI)

Proficiency Testing: A means of evaluating a laboratory's performance under controlled conditions relative to a given set of criteria through analysis of unknown samples provided by an external source. (TNI)

Proficiency Testing Program: The aggregate of providing rigorously controlled and standardized environmental samples to a laboratory for analysis, reporting of results, statistical evaluation of the results and the collective demographics and results summary of all participating laboratories. (TNI)

Proficiency Test Sample (PT): A sample, the composition of which is unknown to the laboratory and is provided to test whether the laboratory can produce analytical results within specified acceptance criteria. (TNI)

Quality Assurance: An integrated system of management activities involving planning, implementation, assessment, reporting and quality improvement to ensure that a process, item or service is of the type of quality needed and expected by the client. (TNI)

Quality Assurance [Project] Plan (QAPP): A formal document describing the detailed quality control procedures by which the quality requirements defined for the data and decisions pertaining to a specific project are to be achieved. (EAP-QAD)

Quality Control: The overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer; operational techniques and activities that are used to fulfill requirements for quality; also the system of activities and checks used to ensure that measurement systems are maintained within prescribed limits, providing protection against "out of control" conditions and ensuring that the results are of acceptable quality. (TNI)

Quality Control Sample: A sample used to assess the performance of all or a portion of the measurement system. One of any number of samples, such as Certified Reference Materials, a quality system matrix fortified by spiking, or actual samples fortified by spiking, intended to demonstrate that a measurement system or activity is in control. (TNI)

Quality Manual: A document stating the management policies, objectives, principles, organizational structure and authority, responsibilities, accountability, and implementation of an agency, organization, or laboratory, to ensure the quality of its product and the utility of its product to its users. (TNI)

Quality System: A structured and documented management system describing the policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for ensuring quality in its work processes, products (items), and services. The quality system provides the framework for planning, implementing, and assessing work performed by the organization and for carrying out required QA and QC activities. (TNI)

Raw Data: The documentation generated during sampling and analysis. This documentation includes, but is not limited to, field notes, electronic data, magnetic tapes, untabulated sample results, QC sample results, print outs of chromatograms, instrument outputs, and handwritten records. (TNI)

Record Retention: The systematic collection, indexing and storing of documented information under secure conditions.

Reference Material: Material or substance one or more properties of which are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials. (TNI)

Reference Standard: Standard used for the calibration of working measurement standards in a given organization or a given location. (TNI)

Sampling: Activity related to obtaining a representative sample of the object of conformity assessment, according to a procedure.

Second Order Polynomial Curve (Quadratic): The 2nd order curves are a mathematical calculation of a slightly curved line over two axis. The y axis represents the instrument response (or Response ratio) of a standard or sample and the x axis represents the concentration. The 2nd order regression will generate a coefficient of determination (COD or r2) that is a measure of the "goodness of fit" of the quadratic curvature the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r2 must be greater than or equal to 0.99.

Selectivity: The ability to analyze, distinguish, and determine a specific analyte or parameter from another component that may be a potential interferent or that may behave similarly to the target analyte or parameter within the measurement system. (TNI)

Sensitivity: The capability of a method or instrument to discriminate between measurement responses representing different levels (e.g., concentrations) of a variable of interest. (TNI)

Spike: A known mass of target analyte added to a blank, sample or sub-sample; used to determine recovery efficiency or for other quality control purposes.

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Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of standard setting and meets the approval requirements of standard adoption organizations procedures and policies. (TNI)
Standard Operating Procedures (SOPs): A written document which details the method for an operation, analysis, or action, with thoroughly prescribed techniques and steps. SOPs are officially approved as the methods for performing certain routine or repetitive tasks. (TNI)
Storage Blank: A blank matrix stored with field samples of a similar matrix (volatiles only) that measures storage contribution to any source of contamination.
Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.
Surrogate compounds must be added to all samples, standards, and blanks, for all organic chromatography methods except when the matrix precludes its use or when a surrogate is not available. Poor surrogate recovery may indicate a problem with sample composition and shall be reported to the client whose sample produced poor recovery. (QAMS)
Systems Audit (also Technical Systems Audit): A thorough, systematic, qualitative on-site assessment of the facilities, equipment, personnel, training, procedures, record keeping, data validation, data management, and reporting aspects of a total measurement system. (EPA-QAD)
Technical Manager: A member of the staff of an environmental laboratory who exercises actual day-to-day supervision of laboratory operations for the appropriate fields of accreditation and reporting of results
Technology: A specific arrangement of analytical instruments, detection systems, and/or preparation techniques.
Traceability: The ability to trace the history, application, or location of an entity by means of recorded identifications. In a calibration sense, traceability relates measuring equipment to national or international standards, primary standards, basic physical constants or properties, or reference materials. In a data collection sense, it relates calculations and data generated throughout the project back to the requirements for the quality of the project. (TNI)
Trip Blank: A blank matrix placed in a sealed container at the laboratory that is shipped, held unopened in the field, and returned to the laboratory in the shipping container with the field samples.
Uncertainty: A parameter associated with the result of a measurement that characterizes the dispersion of the value that could reasonably be attributed to the measured value.

Acronyms:
CAR – Corrective Action Report
CCV – Continuing Calibration Verification
CF – Calibration Factor
CFR – Code of Federal Regulations
COC – Chain of Custody
DOC – Demonstration of Capability
DQO – Data Quality Objectives
DUP - Duplicate
EHS – Environment, Health and Safety
EPA – Environmental Protection Agency
GC - Gas Chromatography
GC/MS - Gas Chromatography/Mass Spectrometry
HPLC - High Performance Liquid Chromatography
ICP - Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP/MS – ICP/Mass Spectrometry
ICV – Initial Calibration Verification
IDL – Instrument Detection Limit
IH – Industrial Hygiene
IS – Internal Standard
LCS – Laboratory Control Sample
LCSD – Laboratory Control Sample Duplicate
LIMS – Laboratory Information Management System
LOD – Limit of Detection
LOQ – Limit of Quantitation
MDL – Method Detection Limit
MDLCK – MDL Check Standard
MDLV – MDL Verification Check Standard
MRL – Method Reporting Limit Check Standard
MS – Matrix Spike
MSD – Matrix Spike Duplicate
SDS - Safety Data Sheet

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NELAP - National Environmental Laboratory Accreditation Program
PT – Performance Testing
TNI – The NELAC Institute
QAM – Quality Assurance Manual
QA/QC – Quality Assurance / Quality Control
QAPP – Quality Assurance Project Plan
RF – Response Factor
RPD – Relative Percent Difference
RSD – Relative Standard Deviation
SD – Standard Deviation
SOP – Standard Operating Procedure
TAT – Turn-Around-Time
VOA – Volatiles
VOC – Volatile Organic Compound

Appendix.6) Analytical Method References
Reference methods include:

- Eastern Environmental Radiation Facility Radiochemistry Procedures Manual, EPA, PB84-215581, June 1984.
- HASL-300 28th Edition, Environmental Measurements Laboratory (EML), 1997.
- Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, Fourth Edition, EPA/600/4-90/027F, August 1993.
- Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, Fifth Edition, EPA-821-R-02-012, October 2002.
- Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Analysis and Sampling Procedures; 40CFR Part 136 as amended by Method Update Rule; August 28, 2017.
- Methods for Chemical Analysis of Water and Wastes, EPA 600 (4-79-020), 1983.
- Methods for the Determination of Inorganic Substances in Environmental Samples, EPA-600/R-93/100, August 1993.
- Methods for the Determination of Metals in Environmental Samples, EPA/600/4-91/010, June 1991. Supplement I: EPA-600/R-94/111, May 1994.
- NIOSH Manual of Analytical Methods, 4th ed., August 1994.
- Statement of Work for Inorganics & Organics Analysis, SOM and ISM, current versions, USEPA Contract Laboratory Program Multi-media, Multi-concentration.
- Standard Methods for the Examination of Water and Wastewater, 18th/19th /20th/ on-line edition; Eaton, A.D. Clesceri, L.S. Greenberg, A.E. Eds; American Water Works Association, Water Pollution Control Federation, American Public Health Association: Washington, D.C.
- Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996; Final Update IV, January 2008; Final Update V, August 2015.
- Annual Book of ASTM Standards, American Society for Testing & Materials (ASTM), Philadelphia, PA.
- National Status and Trends Program, National Oceanographic and Atmospheric Administration, Volume I-IV, 1985-1994.
- Code of Federal Regulations (CFR) 40, Parts 136, 141, 172, 173, 178, 179 and 261

Attachment:
Org Chart (./d4doc/flow/)

EFGS-M-OC-FRM46125 Organization Chart
EFGS-P-DR-SOP2801 Data Review and Validation and Monthly Logbook Reviews
EFGS-P-PM-SOP2815 Contract Review
EFGS-P-PM-SOP40740 Subcontracting Samples
EFGS-P-SH-SOP2793 Shipping and Receiving of Client Samples Using Element LIMS
EFGS-P-SH-SOP41445 Sample Receipt and Log-in Using TALS LIMS
EFGS-P-SP-SOP5147 Homogenization, Subsampling of Solids and Multiphasic Liquids
EFGS-Q-QD-SOP2710 Class 1 Weight Calibration, Balance Verification, Calibration & Maintenance
EFGS-Q-QD-SOP2802 Document Management System

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EFGS-Q-QD-SOP2804 Creation and Control of Standard Operating Procedures
EFGS-Q-QD-SOP2814 Personnel Training and Demonstration of Capability Procedures
EFGS-Q-QD-SOP2819 Control Charting and Measurement Uncertainties
EFGS-Q-QD-SOP2831 Use, Calibration, and Maintenance of Laboratory Thermometers and Refrigerator and Freezer Temperature Monitoring and Maintenance
EFGS-Q-QD-SOP2835 Incident Reports, Out-of-Specification Reports and Client Complaints
EFGS-Q-QD-SOP2989 Quality Assurance Audit Procedures and Monthly QA Reports
EFGS-Q-QD-SOP41922 Receipt, Preparation, Storage and Verification of Standards and Reagents and Traceability Protocols
EFGS-S-HS-QP12066.0004 Chemical Hygiene Plan
EFGS-S-HS-SOP2991 Waste Disposal Procedures for Client Sample Waste
EFGS-S-HS-SOP5670 Health and Safety Evaluation and Auditing
EFGS-S-P-SOP2809 Ordering Laboratory Supplies/Services and Testing Acid and Bottle Lots
EFGS-T-TM-SOP2839 Stock and Prepared Standards
EFQA-Q-QD-SOP2833 Developing Effective Preventive Actions Through Risk Management

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Quality Assurance Manual

Eurofins Chicago
2417 Bond Street
University Park, IL 60484
Phone: 708-534-5200
Fax: 708-534-5211

www.EurofinsUS.com/ENV

Quality Assurance Manual Approval Signatures

Business Unit Manager – Lauren Gillins — Date 3/29/24

Organic Operations Manager –Elliott Rice — Date 2024-03-29

Supervisor, GC, GC/MS Semivolatiles
Gary Rynkar — Date 3/29/24

Supervisor, GC, GC/MS Volatiles
Pete Ricarello — Date 3/29/24

Quality Manager – Nicole Berg — Date 3/29/24

Supervisor, Metals – Debbie Johnson — Date 3/29/24

Supervisor, Wet Chemistry –
Paul Kolarczyk — Date 3/29/24

Supervisor, Sample Receipt/Container Management
Jeff James — Date 3-29-24

EH&S Coordinator – Chris Hoham — Date 4/1/24

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SECTION 2

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SECTION 3

INTRODUCTION SCOPE AND APPLICABILITY

3.1 INTRODUCTION AND COMPLIANCE REFERENCES

Eurofins Chicago's Quality Assurance Manual is a document prepared to define the overall policies, organization objectives and functional responsibilities for achieving the laboratory's QA Program. Governing SOPs are in place within the organization to ensure the proper execution of the QA manual (refer to Appendix 1). This manual and referenced documents are required reading for all personnel.

The laboratory is a ream of people who work together to serve the health and environmental needs of society through science and technology. We maintain a local perspective in its scope of services and client relations and maintain a national perspective in terms of quality.

As such, the QA Manual has been prepared to assure compliance with The NELAC Institute (TNI) Standard, dated 2009 and 2016, and ISO/IEC Guide 17025:2005 and 2017. In addition, the policies and procedures outlined in Appendix 1 are compliant with Eurofins Chicago and the various accreditation and certification programs which are held by the laboratory to support environmental work (Appendix 6). The Quality Assurance Manual provides a summary of Eurofins quality and data integrity system. It contains requirements and general guidelines under which all Eurofins facilities shall conduct their operations.

Refer to Appendix 2 for a list of additional references which this QA Manual is compliant, and Table of Contents for compliance crosswalk of this manual to the TNI & ISO/IEC Guide 17025 requirements.

3.2 TERMS AND DEFINITIONS

A QA Program is a company-wide system designed to ensure that data produced by the laboratory conforms to the standards set by state and/or federal regulations. The program functions at the management level through company goals, from guidance at the executive management level, and at the analytical level through Standard Operating Procedures (SOPs) and quality control. Our program is designed to minimize systematic error, encourage constructive, documented problem solving, and provide a framework for continuous improvement within the organization to better serve our clients.

Refer to Appendix 5 for a list of Terms and Acronyms.

3.3 SCOPE / FIELDS OF TESTING

The laboratory analyzes a broad range of environmental and industrial samples. Sample matrices vary among drinking water, surface water, groundwater, effluent water, leachates, wastewater, soil, sediment, hazardous waste, sludge, ash, paint chips, filters, wipes, waste and tissue. The QA Program contains specific procedures and methods to test samples of differing matrices for chemical, physical and biological parameters. The Program also contains guidelines on maintaining documentation of analytical processes, reviewing results, servicing clients and tracking samples through the laboratory. The technical and service requirements of all analytical requests are thoroughly evaluated before commitments are made to accept the work. Measurements are made using published reference methods or methods developed and validated by the laboratory.

The methods covered by this manual include the most frequently requested methodologies needed to provide analytical services in the United States and its territories and Canada. The

specific list of test methods used by the laboratory can be found in Appendix 8. Our areas of expertise include:

Standard Services
• Volatiles • Semivolatiles • Metals • Pesticides/PCBs/Herbicides • Petroleum Hydrocarbons • Waste Characterization • Non-Potable Water Testing • Drinking Water Testing • Soil and Surface Water Testing

NOTE: All current certificates and scopes of accreditation are available on the laboratory's website.

The approach of this manual is to define the minimum level of quality assurance and quality control necessary to meet requirements. All methods performed by the laboratory shall meet these criteria as appropriate. In some instances, quality assurance project plans (QAPPs), project specific data quality objectives (DQOs) or local regulations may require criteria other than those contained in this manual. In these cases, the laboratory will abide by the requested criteria following review and acceptance of the requirements by the Laboratory Director, Project Manager and the QA Manager. In some cases, QAPPs and DQOs may specify less stringent requirements. The Laboratory Director and the QA Manager must determine if it is in the lab's best interest to follow the less stringent requirements.

3.4 MANAGEMENT OF THE MANUAL

3.4.1 Review Process

The template on which this manual is based is reviewed annually by Eurofins National Divisional Support Center (NDSC) which houses the Quality Assurance Leadership team for Eurofins Environment Testing America. NDSC QA will assure that the template remains in compliance with Section 3.1. This manual itself is reviewed annually by senior laboratory management to assure that it reflects current practices and meets the requirements of the laboratory's clients and regulators as well as the QMP. Occasionally, the manual may need changes in order to meet new or changing regulations and operations. The QA Manager will review the changes in the normal course of business and incorporate changes into revised sections of the document. All updates will be reviewed by the senior laboratory management staff. The laboratory updates and approves such changes according to our Document Control & Updating procedures; furthermore, laboratory-specific QAM and SOP changes are approved and documented as detailed in the following SOP: *UP-QA-042*_SOP Signature Authority and Document Control.

SECTION 4

MANAGEMENT AND RESPONSIBILITIES

4.1 OVERVIEW

The laboratory is a local operating unit of Eurofins Environmental Testing. The laboratory's operational and support staff have the day-to-day independent operational authority under the direction of the Laboratory Director, Operations Manager, Department Managers, Technical Director, QA Manager and is supported by the NDSC QA team. The laboratory management staff includes directors, managers and group leaders. The organizational chart of the

management staff are presented in figure 4-1. Individual department staff lists are maintained in the laboratory's internal intranet.

4.2 ROLES AND RESPONSIBILITIES

In order for the QA Program to function properly, all members of the staff must clearly understand and meet their individual responsibilities as they relate to the quality program. The following descriptions define each role in its relationship to the quality program. The responsibility for quality resides with every employee of the laboratory. All employees have access to the QA Manual, are trained to this manual, and are responsible for upholding the standards therein. Each person carries out his/her daily tasks impartially and in a manner consistent with the goals and in accordance with the procedures in this manual and the laboratory's SOPs. The following descriptions briefly define each role in its relationship to the Quality Assurance Program.

4.2.1 Vice President of Quality and Environmental Health and Safety (VP-QA/EHS)

The Vice President (VP) of QA/EHS reports directly to Eurofins Environment Testing America Chief Operating Officer (COO). With the aid of the NDSC Quality Team Members, Business Unit Managers, Laboratory Directors, the VP-QA/EHS has the responsibility for the establishment, general overview and maintenance of the Quality Assurance and EH&S Programs within Eurofins Environment Testing America. Additional responsibilities include:

- Review of QA/QC and EHS aspects of NDSC Official Document, national projects and expansions or changes in services.
- Work with various organizations outside of the laboratory to further the development of quality standards and represent the laboratory at various trade meetings.
- Prepare monthly reports for quality and EH&S metrics across the environmental testing laboratories and a summary of any quality and EH&S related initiatives and issues.
- With the assistance of the Executive Management, and the EHS Managers, maintenance and implementation of the Eurofins Environment Testing America Environmental, Health and Safety Program.

4.2.2 Quality Directors

There are four (4) Quality Directors within NDSC that report directly to the VP-QA/EHS. These Quality Directors have oversight of the general overview and maintenance of the QA Program within the Eurofins Environment Testing America laboratories. Supported tasks include:

- Monitors laboratory internal audit findings;
- Identifies common laboratory weaknesses and monitors corrective action closures.
- Develops NDSC quality guidance documents and management tools for ensuring and improving compliance;
- Monitors and communicates DoD/DoE requirements;
- Monitors and communicates regulatory and certification requirements;
- Training and OnBoarding
- Laboratory assessments, mentoring, and interventions
- Track/drive root cause investigations and corrective action plans
- Builds knowledge base for preventive actions

4.2.3 Quality Information Manager

The Quality Information works directly with the NDSC Quality Directors and EHS Managers; and reports directly to the VP-QA/EHS. The Quality Information Manager is responsible for the management of:

- NDSC Official Documents
- TALS/LIMS Certification Module Data
- Company's Intranet website
- Company's Regulatory Limits Database
- Subcontract laboratory and approved vendor information
- Internal and External client support for various company groups (e.g., Client Services, EH&S, Legal, IT, Sales) for both quality and operational functions
- Communicate regulatory information and lists

4.2.4 Environmental Health and Safety (EH&S) Managers

There are 3 EH&S Managers within NDSC that report directly to the VP-QA/EHS. These EH&S Managers have oversight of the general overview and maintenance of the EH&S Program within the Eurofins Environment Testing America laboratories. Supported tasks include:

- Consolidation and tracking all safety and health-related information and reports for the company, and managing compliance activities for Eurofins Environment Testing America locations.
- Coordination/preparation of the Environmental, Health and Safety Manual Template that is used by each laboratory to prepare its own laboratory-specific Safety Manual/ CHP.
- Preparation of information and training materials for laboratory EHS Coordinators.
- Assistance in the coordination of employee exposure and medical monitoring programs to insure compliance with applicable safety and health regulations.
- Serving as Department of Transportation (D.O.T.) focal point and providing technical assistance to location management.
- Serving as Hazardous Waste Management main contact and providing technical assistance to location management.

4.2.5 Ethics and Compliance Officers (ECOs)

- The NDSC VP-QA/EHS and Corporate Counsel are Ethics and Compliance Officer (ECO). Each ECO acts as a back-up to the other ECO and both are involved when data investigations occur. Each ECO has a direct line of communication to the entire executive management personnel and lab management staff.
- The ECOs monitor and audit procedures to determine compliance with policies and to make recommendations for policy enhancements to the President, COO, Laboratory Director or other appropriate individuals within the laboratory. The ECO will assist the laboratory QA Manager in the coordination of internal auditing of ethical policy related activities and processes within the laboratory, in conjunction with the laboratory's regular internal auditing function.
- The ECOs will also participate in investigations of alleged violations of policies and work with the appropriate internal departments to investigate misconduct, remedy the situation, and prevent recurrence of any such activity.

4.2.6 Laboratory Director

The Laboratory Director is responsible for the overall quality, safety, financial, technical, human resource and service performance of the whole laboratory and reports to their respective VPO. The Laboratory Director is also responsible for any service centers connected with their laboratory that perform analytical tests, such as short holding time analyses for pH. The Laboratory Director provides the resources necessary to implement and maintain an effective and comprehensive Quality Assurance and Data Integrity Program.

The Laboratory Director, with the assistance of the Quality Assurance Manager, has the overall responsibility for establishing policies that ensure the quality of analytical services meet our client's expectations. These policies are defined in this QAM.

Specific responsibilities include, but are not limited to:

- Provides one or more technical managers for the appropriate fields of testing. If the Technical Manager is absent for a period of time exceeding 15 consecutive calendar days, the Laboratory Director must designate another full time staff member meeting the qualifications of the Technical Manager to temporarily perform this function. If the absence exceeds 35 consecutive calendar days, the primary accrediting authority must be notified in writing.
- Ensures that all analysts and supervisors have the appropriate education and training to properly carry out the duties assigned to them and ensures that this training has been documented.
- Ensures that personnel are free from any commercial, financial and other undue pressures which might adversely affect the quality of their work.
- Ensures company human resource policies are adhered to and maintained.
- Ensures that sufficient numbers of qualified personnel are employed to supervise and perform the work of the laboratory.
- Ensures that appropriate corrective actions are taken to address analyses identified as requiring such actions by internal and external performance or procedural audits. Procedures that do not meet the standards set forth in the QAM or laboratory SOPs may be temporarily suspended by the Laboratory Director.
- Reviews and approves all SOPs prior to their implementation and ensures all approved SOPs are implemented and adhered to.
- Pursues and maintains appropriate laboratory certification and contract approvals. Supports ISO 17025 requirements.
- Ensures client specific reporting and quality control requirements are met.
- Contributes to the continuous improvement of the laboratory operations.
- Maintains an awareness of technical developments and regulatory requirements.
- Captains the management team, consisting of the QA Manager, the Technical Manager(s), and the Operations Manager as direct reports.
- Interfaces with Project Management and Customer Service to forecast receipts, provide quality analytical data to clients and meet on-time delivery dates.
- Communicates facility-specific goals and objectives to employees. Communicates and implements company initiatives designed to foster teamwork and communication.
- Ensures that the facility has appropriate Information Technology resources and that they are being used effectively to support operational requirements.

- Actively participates in the process of sharing and adopting best practices within the company. Provides technical assistance to other Eurofins laboratories as needed to improve productivity and customer service.
- Prioritizes the activities of the operations groups to ensure key goals are achieved and customer service needs are addressed.
- Capital forecasting and instrument life cycle planning for second generation methods and instruments
- Has financial profit/loss responsibility for laboratory, which includes monitoring/approving expenses, personnel hires and providing weekly revenue and profit forecasts to the parent company.

4.2.7 Quality Assurance (QA) Manager or Designee

The QA Manager has responsibility and authority to ensure the continuous implementation of the quality system at the laboratory where they work. The QA Manager is also responsible for any service centers connected with their laboratory that perform analytical tests, such as short holding time analyses for pH.

The QA Manager reports directly to the Laboratory Director and their NDSC Quality Director. This position is able to evaluate data objectively and perform assessments without outside (e.g., managerial) influence. The NDSC QA Team may be used as a resource in dealing with regulatory requirements, certifications and other quality assurance related items. The QA Manager directs the activities of the QA officer to accomplish specific responsibilities, which include, but are not limited to:

- Serves as the focal point for QA/QC in the laboratory.
- Have functions independent from laboratory operations for which he/she has quality assurance oversight.
- Have documented training and/or experience in QA/QC procedures and the laboratory's Quality System.
- Have a general knowledge of the analytical test methods for which data audit/review is performed (and/or having the means of getting this information when needed).
- Arrange for or conducting internal audits on quality systems and the technical operation
- Notifying laboratory management of deficiencies in the quality system and ensuring corrective action is taken. Procedures that do not meet the standards set forth in the QA Manual or laboratory SOPs shall be investigated following procedures outlined in Section 14 and if deemed necessary may be temporarily suspended during the investigation.
- Maintaining and updating the QA Manual.
- Monitoring and evaluating laboratory certifications; scheduling proficiency testing samples.
- Monitoring and communicating regulatory changes that may affect the laboratory to management.
- Training and advising the laboratory staff on quality assurance/quality control procedures that are pertinent to their daily activities.
- The laboratory QA Manager will maintain records of all ethics-related training, including the type and proof of attendance.
- Maintain, improve, and evaluate the corrective action database and the corrective and preventive action systems.

- Objectively monitor standards of performance in quality control and quality assurance without outside (e.g., managerial) influence.
- Coordinating of document control of SOPs, MDLs, control limits, and miscellaneous forms and information.
- Performing technical data audits and method audits to ensure consistency and compliance with regulatory requirements.
- Review of external audit reports and data validation requests.
- Follow-up with audits to ensure client QAPP requirements are met.
- Establishment of reporting schedule and preparation of various quality reports for the Laboratory Director, clients and/or NDSC QA Team.
- Development of suggestions and recommendations to improve quality systems.
- Research of current state and federal requirements and guidelines.
- Participate in the vendor and supplier approval process, including subcontractors.
- Captains the QA team to enable communication and to distribute duties and responsibilities.
- Communication to the relevant regulatory authorities when there are management or facility changes that impact the laboratory.
- Ensuring communication & monitoring standards of performance to ensure that systems are in place to produce the level of quality as defined in this document.
- Evaluation of the thoroughness and effectiveness of training.
- Compliance with ISO 17025

4.2.8 Network Administrator

The Network Administrator reports directly to the Regional Supervisor.

The overall role of the Information Technology (IT) Administrator is to enhance laboratory productivity through improved information access, flow, and security. For information to be of greatest value, it must be readily accessible and reliable. It is the responsibility of the IT Administrator to provide software tools that allow quick and user friendly access to that information, while at the same time controlling access to that information to those that have the need and proper authority.

Information flow can be enhanced through automation. Automation is the minimization of human intervention in a process. Reduction in human intervention can result in significant error reductions and time savings. The IT Administrator assists the laboratory in automation by providing hardware and software solutions to help minimize human intervention in data collection, processing, and storage.

The IT Administrator is responsible for providing data security by controlling access, as mentioned above, and for providing for disaster recovery. Data stored on the central Eurofins Laboratory Information Management System (LIMS) is the direct responsibility of IT. No fewer than two copies of all data should exist at any time so that lost or destroyed data can always be retrieved from an alternate source. These copies may consist of data within the system and on magnetic tape in the case of live data, or two copies on magnetic tape for archived data or another hard disk.

Corporate IT duties are:

- Maintains the Eurofins laboratory information system (LIMS) for tracking all samples in the laboratory.

- Maintains historical files of software, software operating procedures (manuals), software changes/modifications (Change Log) and software version numbers.
- Maintains log of repairs and service performed on LIMS hardware.
- Verifies security practices to assure the integrity of LIMS data. Identifies threats, potential threats, and future threats.
- Maintains awareness of any environmental conditions of the facility housing the LIMS that may compromise LIMS raw data and informs management.
- LIMS database back-up.

4.2.9 Technical Manager or Designee

The Technical Manager(s) reports directly to the Laboratory Director. He/she is accountable for all analyses and analysts under their experienced supervision and for compliance with the ISO 17025:2017 Standard. The scope of responsibility ranges from the new-hire process and existing technology through the ongoing training and development programs for existing analysts and new instrumentation. Specific responsibilities include, but are not limited to:

- Exercises day-to-day supervision of laboratory operations for the appropriate field of accreditation and reporting of results. Coordinating, writing, and reviewing preparation of all test methods, i. e., SOPs, with regard to quality, integrity, regulatory and optimum and efficient production techniques, and subsequent analyst training and interpretation of the SOPs for implementation and unusual project samples. He/she insures that the SOPs are properly managed and adhered to at the bench. He/she develops standard costing of SOPs to include supplies, labor, overhead, and capacity (design vs. demonstrated versus first-run yield) utilization.
- Reviewing and approving, with input from the QA Manager, proposals from marketing, in accordance with an established procedure for the review of requests and contracts. This procedure addresses the adequate definition of methods to be used for analysis and any limitations, the laboratory's capability and resources, the client's expectations. Differences are resolved before the contract is signed and work begins. A system documenting any significant changes is maintained, as well as pertinent discussions with the client regarding their requirements or the results of the analyses during the performance of the contract. All work subcontracted by the laboratory must be approved by the client. Any deviations from the contract must be disclosed to the client. Once the work has begun, any amendments to the contract must be discussed with the client and so documented.
- Monitoring the validity of the analyses performed and data generated in the laboratory. This activity begins with reviewing and supporting all new business contracts, insuring data quality, analyzing internal and external non-conformances to identify root cause issues and implementing the resulting corrective and preventive actions, facilitating the data review process (training, development, and accountability at the bench), and providing technical and troubleshooting expertise on routine and unusual or complex problems.
- Providing training and development programs to applicable laboratory staff as new hires and, subsequently, on a scheduled basis. Training includes instruction on calculations, instrumentation management to include troubleshooting and preventive maintenance.
- Enhancing efficiency and improving quality through technical advances and improved LIMS utilization. Capital forecasting and instrument life cycle planning for second generation methods and instruments as well as asset inventory management.
- Coordinating sample management from "cradle to grave," insuring that no time is lost in locating samples.
- Scheduling all QA/QC-related requirements for compliance, e.g., MDLs, etc.

- Captains department personnel to communicate quality, technical, personnel, and instrumental issues for a consistent team approach.
- Coordinates audit responses with the QA Manager.
- Compliance with ISO 17025.

4.2.10 Operations Manager

The Operations Manager manages and directs the analytical production sections of the laboratory. She reports directly to the Laboratory Director. She assists the Technical Manager in determining the most efficient instrument utilization. More specifically, he/she:

- Evaluates the level of internal/external non-conformances for all departments.
- Continuously evaluates production capacity and improves capacity utilization.
- Continuously evaluates turnaround time and addresses any problems that may hinder meeting the required and committed turnaround time from the various departments.
- Develops and improves the training of all analysts in cooperation with the Technical Manager and QA Manager and in compliance with regulatory requirements.
- Works with the Preventive Maintenance Coordinator to ensure that scheduled instrument maintenance is completed.
- Is responsible for efficient utilization of supplies.
- Constantly monitors and modifies the processing of samples through the departments.
- Fully supports the quality system and, if called upon in the absence of the QA Manager, serves as his substitute in the interim.

4.2.11 Project Manager (PM)

Members of the laboratory Client Services/Project Management Group are responsible for organizing and managing client projects. Clients are assigned a project manager who serves as their primary contact at the laboratory. It is the PM's responsibility to act as the client advocate by communicating client requirements to laboratory personnel and ensuring that clients provide complete information needed by the laboratory to meet those requirements – including all verbal communication.

- Scheduling sample submissions, sample container orders and sample pick-up via the laboratory courier service.
- Confirming certification status
- Coordinating and communicating turnaround time (TAT) requirements for high priority samples/projects.
- Answering common technical questions, facilitating problem resolution and coordinating technical details with the laboratory staff.
- Ensuring that client specifications, when known, are met by communicating project and quality assurance requirements to the laboratory.
- Notifying the supervisors of incoming projects and sample delivery schedules.
- Accountable to clients for communicating sample status reports or results prior to receipt of the final report.
- Monitor the status of all data package projects in-house to ensure timely and accurate delivery of reports.
- Inform clients of data package-related problems and resolve service issues.

4.2.12 Department Supervisors

Supervisors report to the Laboratory Director or Operations Manager. Each one is responsible to:

- Ensure that analysts in their department adhere to applicable SOPs and the QA Manual. They perform frequent SOP and QA Manual review to determine if analysts are in compliance and if new, modified, and optimized measures are feasible and should be added to these documents.
- With regard to analysts, participates in the selection, training (as documented in Section 5.3), development of performance objectives and standards of performance, appraisal (measurement of objectives), scheduling, counseling, discipline, and motivation of analysts and documents these activities in accordance with systems developed by the QA and Personnel Departments. They evaluate staffing sufficiency and overtime needs. Training consists of familiarization with SOP, QC, Safety, and computer systems.
- Encourage the development of analysts to become cross-trained in various methods and/or operate multiple instruments efficiently while performing maintenance and documentation, self-supervise, and function as a department team.
- Provide guidance to analysts in resolving problems encountered daily during sample prep/analysis in conjunction with the Technical Manager, Operations Manager, and/or QA Manager. Each is responsible for 100% of the data review and documentation, non-conformance and *CPAR* issues, the timely and accurate completion of performance evaluation samples and MDLs, for his department.
- Ensure all logbooks are maintained, current, and properly labeled or archived.
- Report all non-conformance conditions to the QA Manager, Technical Manager, Operations Manager, and/or BU / Laboratory Director.
- Ensure that preventive maintenance is performed on instrumentation as detailed in the QA Manual or SOPs. He is responsible for developing and implementing a system for preventive maintenance, troubleshooting, and repairing or arranging for repair of instruments.
- Maintain adequate and valid inventory of reagents, standards, spare parts, and other relevant resources required to perform daily analysis.
- Achieve optimum turnaround time on analyses and compliance with holding times.
- Conduct efficiency and cost control evaluations on an ongoing basis to determine optimization of labor, supplies, overtime, first-run yield, capacity (designed vs. demonstrated), second- and third-generation production techniques/instruments, and long-term needs for budgetary planning.
- Develop, implement, and enhance calibration programs.
- Provide written responses to external and internal audit issues.

4.2.13 Laboratory Analysts

Laboratory analysts are responsible for conducting analysis and performing all tasks assigned to them by the group leader or supervisor. The responsibilities of the analysts are listed below:

- Perform analyses by adhering to analytical and quality control protocols prescribed by current SOPs, this QA Manual, and project-specific plans honestly, accurately, timely, safely, and in the most cost-effective manner.
- Document standard and sample preparation, instrument calibration and maintenance, data calculations, sample matrix effects, and any observed non-conformance on worklists, benchsheets, lab notebooks and/or the Non-Conformance Database.

- Report all non-conformance situations, instrument problems, matrix problems and QC failures, which might affect the reliability of the data, to their supervisor, the Technical Manager, and/or the QA Manager or member of QA staff.
- Perform 100% review of the data generated prior to entering and submitting for secondary level review.
- Suggest method improvements to their supervisor, the Technical Manager, and the QA Manager. These improvements, if approved, will be incorporated. Ideas for the optimum performance of their assigned area, for example, through the proper cleaning and maintenance of the assigned instruments and equipment, are encouraged.
- Work cohesively as a team in their department to achieve the goals of accurate results, optimum turnaround time, cost effectiveness, cleanliness, complete documentation, and personal knowledge of environmental analysis.

4.2.14 Field Sampling/Courier/Shipping Manager/Sample Archiving

The Field Sampling/Courier/Shipping/Sample Login Manager reports directly to the Laboratory Director. He is responsible for:

- Coordinating of sampling events for compliance monitoring including field measurements
- Scheduling all courier sample pickups based on client's needs
- Supervise the timely and correct shipment of sample containers, including proper preservatives and instructions to the clients.
- Maintaining accurate records of sample container shipments
- The organized storage and appropriate climate control of samples

4.2.15 Environmental Health & Safety Coordinator (EHSC)

The Environmental Health & Safety Coordinator (EHSC) reports to the Laboratory Director and the EH&S Director and ensures that systems are maintained for the safe operation of the laboratory.

The EHSC is responsible for the safety and well-being of all employees while at the laboratory. This includes, but is not limited to, administering the Corporate Safety Manual that complies with federal regulations, SDS training and review, conducting laboratory safety orientation and tours for all new employees, providing instructions on safety equipment, cleaning up laboratory spills, and instructing personnel of laboratory procedures for emergency situations. The Health and Safety Coordinator is on-call 24-hours a day, 7-days a week for all laboratory situations.

The EHSC responsibilities additionally include waste management of laboratory generated hazardous waste in accordance with appropriate regulations. This includes maintenance of required documentation, such as waste manifests, segregation of waste in accordance with requirements, and training of personnel in proper segregation of waste.

- Enforce the EH&S program and the requirements of the manual in conjunction with the EHSC
- Act as the facility CHO or HCO per the OSHA regulations.
- Be knowledgeable in the regulations that affect EH&S at the facility where they work.
- Coordinate the investigation of all accidents and incidents.
- Maintain statistics on accidents and injuries. Review the annual reporting of the OSHA 300 Log for correctness, have the Facility/Laboratory Director sign it and ensure it is posted as required.
- Note: The OSHA 300 is a log of work-related injuries and illnesses that have occurred over the calendar year. The log must be posted between February 1st and April 30th of each year.
- Assure that accidents are reported and Workers Compensation requirements are followed.

- Approve safety aspects listed in technical method standard operating procedures.
- Ensure a current chemical inventory of list of chemicals that are used is maintained. The inventory should be reviewed and updated annually.
- Ensure manufacturers' Safety Data Sheets (SDSs) are current and readily available to all employees.
- Conduct reviews of chemical usage in the facility to assess the potential for exposure to chemical, physical and biological hazards, the need for workplace monitoring, and compliance with environmental regulations.
- Conduct and/or coordinate industrial hygiene activities.
- Coordinate emergency response activities for the facility.
- Ensure that appropriate PPE is available and employees are properly trained in its use.
- Ensure that training specified in the NDSC HSE Manual (NDSC-US EHS-QP46060) is provided for all employees; that this training is documented and that make-up sessions are available. Participate in discussions of safety matters that relate to the design of new or rehabilitated facilities.
- Oversee installation of safety equipment upgrades or modifications to ensure safe working conditions.
- Forward suggestions for improving the Company's EH&S program to the VP-Quality & EHS.
- Ensure that adequate quarterly inspections are conducted of the main work areas. Office areas should be inspected at least once every year.
- Ensure that inspections of emergency equipment and fume hoods are performed within the required time period.
- Investigate non-conformances and violations of regulations and Company policies regarding environmental and safety issues.
- Accompany an EH&S Manager on annual audit for one of the operations within at least 3-months of when they are appointed to the position, or review the latest EH&S audit report and findings covering the EHSC's home facility with the EHSM.
- Conduct internal audits for compliance with regulations and Company policies. Implement a system to assure proper tracking and closure of audit findings.
- Submit a monthly report of environmental and safety activities to the VP-Quality & EHS.
- Act as a designated contact with local regulatory agencies in matters relating to environmental health and safety.

4.2.16 Hazardous Waste Coordinator

The Hazardous Waste Coordinator reports directly to the Laboratory Director. The duties consist of:

- Reviewing and updating annually the Hazardous Waste Contingency Plan in the Environmental Health & Safety Manual.
- Auditing the staff with regard to compliance with the Hazardous Waste Contingency Plan.
- Ensure that the hazardous waste program meets regulatory requirements.
- Ensure that hazardous materials shipments meet regulatory requirements.
- Ensure that a waste minimization program is developed and implemented as required under any Federal or State regulations for the facility. It must be noted that this is not required for Small Quantity Generators or Conditionally Exempt Small Quantity Generators. In some case, operations may be able to obtain exemptions from their state for this requirement.

4.2.17 Facilities Maintenance/Sample Disposal

The Facilities Maintenance Manager reports directly to the Laboratory Director. He is responsible for the following:

- Managing facility maintenance.
- Supervising the disposal of samples in accordance with the Waste Disposal SOP, the Hazardous Waste Contingency Plan in the Chemical Hygiene/Safety Manual, and the U. S. Department of Agriculture requirements.

4.3 BUSINESS CONTINUITY AND CONTINGENCY PLANS

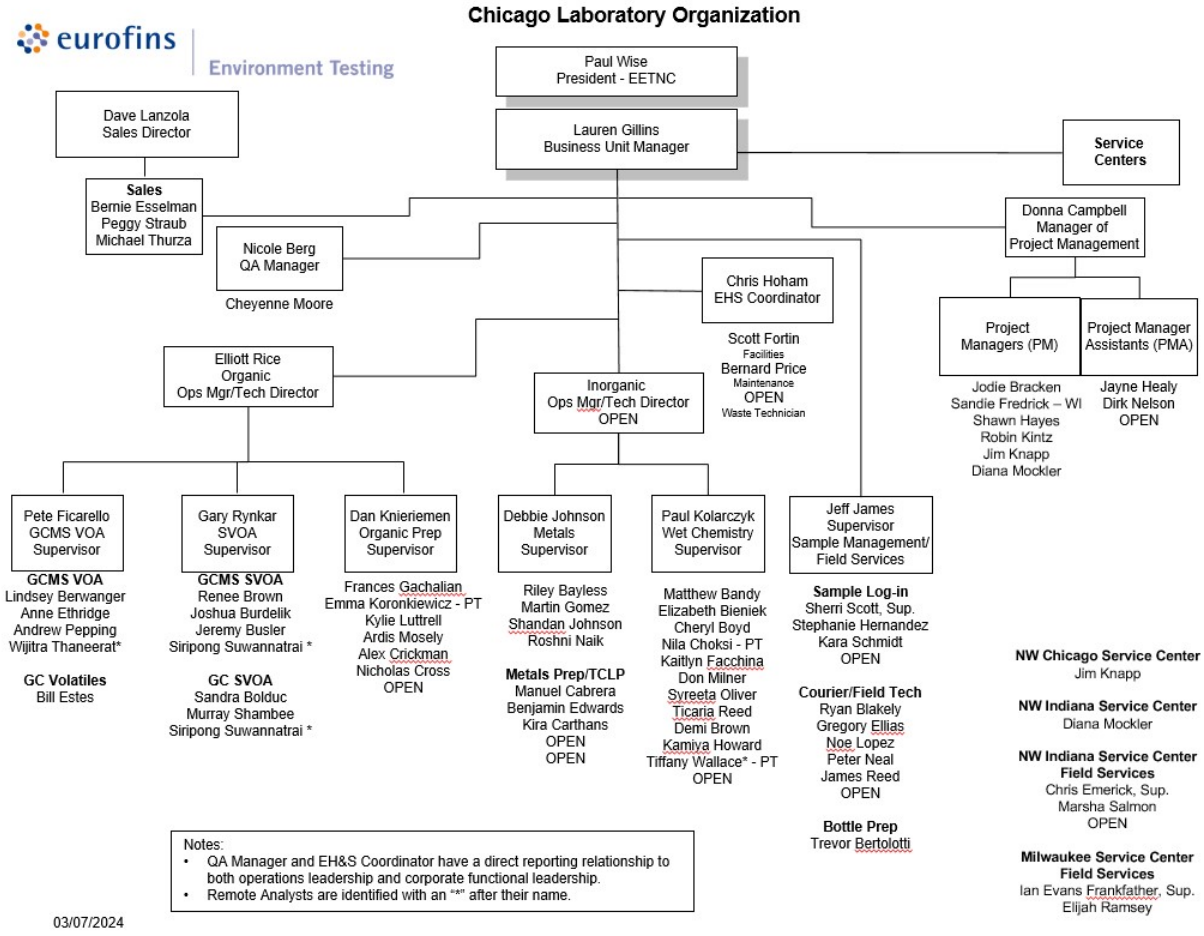
Various policies and practices are in place to address continuity of business and contingency plans to ensure continued operations or minimal disruption in operations should unplanned events (natural disasters, unexpected management changes, etc.) occur. Deputies are identified for all key management personnel. Deputies would temporarily fill a role if the primary is absent for more than 15 consecutive calendar days. The deputies must meet the same qualifications as the primary person should they be required to take on the responsibilities. The QA Manager communicates to the relevant regulatory authorities when there are management or facility changes that impact the laboratory. Changes in the technical director must be communicated within a period of time and in the manner dictated by each regulatory authority

The following table defines who assumes the responsibilities of key personnel in their absence:

Key Personnel	Deputy	Comment
Laboratory Director – Lauren Gillins	Elliott Rice Chris Hoham	Client / Quote Facility
Project Management – Donna Cambell	Sandie Fredrick Shawn Hayes Robin Kintz Diana Mockler Jim Knapp	PM PM PM PM PM
QA Manager – Nicole Berg	Cheyenne Moore	QA Specialist
Organic Operations Manager – Elliott Rice	Pete Ficarello Gary Rynkar Dan Knieriemen Debbie Johnson Paul Kolarczyk	Supervisor – GC VOA / MS VOA Supervisor – GC SVOA / GCMS SVOA Supervisor – Organic Extractions Supervisor – Metals Supervisor – Wet Chemistry
EH&S Coordinator – Chris Hoham	Jeff James	Supervisor – Sample Management Corporate EH&S Manager
Data Management – Jane Healy	Jodi Bracken	Specialist – Data Management
Sample Management / Bottle Prep – Jeff James	Sherri Scott Trevor Bertolotti	Login Bottle Prep

Figure 4-1.

Eurofins Chicago Organization Chart



SECTION 5

PERSONNEL

5.1 OVERVIEW

The laboratory's management believes that its highly qualified and professional staff is the single most important aspect in assuring a high level of data quality and service. The staff consists of professionals and support personnel.

All personnel must demonstrate competence in the areas where they have responsibility. Any staff that is undergoing training shall have appropriate supervision until they have demonstrated their ability to perform their job function on their own. Staff shall be qualified for their tasks based on appropriate education, training, experience and/or demonstrated skills as required.

The laboratory employs sufficient personnel with the necessary education, training, technical knowledge and experience for their assigned responsibilities.

All personnel are responsible for complying with all QA/QC requirements that pertain to the laboratory and their area of responsibility. Each staff member must have a combination of experience and education to adequately demonstrate a specific knowledge of their particular area of responsibility. Technical staff must also have a general knowledge of lab operations, test methods, QA/QC procedures and records management.

Laboratory management is responsible for formulating goals for lab staff with respect to education, training and skills and ensuring that the laboratory has a policy and procedures for identifying training needs and providing training of personnel. The training shall be relevant to the present and anticipated responsibilities of the lab staff.

The laboratory only uses personnel that are employed by or under contract to, the laboratory. Contracted personnel, when used, must meet competency standards of the laboratory and work in accordance to the laboratory's quality system.

5.2 EDUCATION AND EXPERIENCE REQUIREMENTS FOR TECHNICAL STAFF

The laboratory makes every effort to hire analytical staff that possesses a college degree (AA, BA, BS) in an applied science with some chemistry in the curriculum. Exceptions can be made based upon the individual's experience and ability to learn. There are competent analysts and technicians in the industry who have not earned a college degree. Selection of qualified candidates for laboratory employment begins with documentation of minimum education, training, and experience prerequisites needed to perform the prescribed task. Minimum education and training requirements for laboratory employees are outlined in job descriptions maintained by Eurofins Environment Testing America Human Resources.

Experience and specialized training are occasionally accepted in lieu of a college degree (basic lab skills such as using a balance, aseptic or quantitation techniques, etc. are also considered).

As a general rule for analytical staff:

Specialty	Education	Experience
Extractions, Digestions, some electrode methods (pH, DO etc.), or Titrimetric and Gravimetric Analyses	H.S. Diploma	On the job training (OJT)

Specialty	Education	Experience
CVAA, Single component or short list GC Chromatography (e.g. BTEX-GC, IC)	A college degree in an applied science or 2 years of college and at least 1 year of college chemistry	or 2 years prior analytical experience is required
ICP, ICPMS, Long List or complex Chromatography (e.g., Pesticides, PCB, Herbicides, Fuels), GCMS	A college degree in an applied science or 2 years of college chemistry	or 5 years of prior analytical experience
Spectra Interpretation	A college degree in an applied science or 2 years of college chemistry	And 2 years relevant experience or 5 years of prior analytical experience
Technical Managers – General	Bachelors Degree in an applied science or engineering with 24 semester hours in chemistry An advanced (MS, PhD.) degree may substitute for one year of experience	And 2 years experience in environmental analysis of representative analytes for which they will oversee
Technical Managers – Wet Chemistry only (no advanced instrumentation)	Associates degree in an applied science or engineering or 2 years of college with 16 semester hours in chemistry	And 2 years relevant experience

When an analyst does not meet these requirements, they can perform a task under the direct supervision of a qualified analyst, peer reviewer or Technical Manager, and are considered an analyst in training. The person supervising an analyst in training is accountable for the quality of the analytical data and must review and approve data and associated corrective actions.

5.3 TRAINING

The laboratory is committed to furthering the professional and technical development of employees at all levels.

Orientation to the laboratory's policies and procedures, in-house method training, and employee attendance at outside training courses and conferences all contribute toward employee proficiency. Below are examples of various areas of required employee training:

Required Training	Time Frame*	Employee Type
Environmental Health & Safety	Prior to lab work	All
Ethics – New Hires	1 week of hire	All
Ethics – Comprehensive	60 days of hire	All
Data Integrity	60 days of hire	Technical and PMs
Quality Assurance	90 days of hire	Technical and PMs
Ethics – Comprehensive Refresher	Annually	All
Initial Demonstration of Capability (IDOC)	Prior to unsupervised method performance	Technical
Continuing Demonstration of Capability (CDOC)	Annually	Technical

The laboratory maintains records of relevant authorization/competence, education, professional qualifications, training, skills and experience of technical personnel (including contracted personnel) as well as the date that approval/authorization was given. These records are kept on file at the laboratory. Also refer to "Demonstration of Capability" in Section 19.

The training of technical staff is kept up to date by:

- Each employee must have documentation in their training file that they have read, understood and agreed to follow the most recent version of the laboratory QA Manual and SOPs in their area of responsibility. This documentation is updated as SOPs are updated.
- Documentation from any training courses or workshops on specific equipment, analytical techniques or other relevant topics.
- Documentation of proficiency (refer to Section 19).
- An Ethics Agreement signed by each staff member (renewed each year) and evidence of annual ethics training.
- A Confidentiality Agreement signed by each staff member signed at the time of employment.
- Human Resources maintains documentation and attestation forms on employment status & records; benefit programs; timekeeping/payroll; and employee conduct (e.g., ethics violations). This information is maintained in the employee's secured personnel file.

Evidence of successful training could include such items as:

- Adequate documentation of training within operational areas, including one-on-one technical training for individual technologies, and particularly for people cross-trained.
- Analysts knowledge to refer to QA Manual for quality issues.
- Analysts following SOPs, i.e., practice matches SOPs.
- Analysts regularly communicate to supervisors and QA if SOPs need revision, rather than waiting for auditors to find problems.

For additional details on the laboratory's training program refer to the laboratory SOP *UP-QA-014*, Training Program: Mechanisms and Documentation Processes Defined by Operational Assessment.

5.4 DATA INTEGRITY AND ETHICS TRAINING PROGRAM

The laboratory's Ethics and Data Integrity Program is discussed in Section 7.2. Employees are trained as to the legal and environmental repercussions that result from data misrepresentation. Key topics covered in the presentation include:

- Organizational mission and its relationship to the critical need for honesty and full disclosure in all analytical reporting.
- Ethics Policy
- How and when to report ethical/data integrity issues. Confidential reporting.
- Record keeping.
- Discussion regarding data integrity procedures.
- Specific examples of breaches of ethical behavior (e.g. peak shaving, altering data or computer clocks, improper macros, etc., accepting/offering kickbacks, illegal accounting practices, unfair competition/collusion)
- Internal monitoring. Investigations and data recalls.
- Consequences for infractions including potential for immediate termination, debarment, or criminal prosecution.
- Importance of proper written narration / data qualification by the analyst and project manager with respect to those cases where the data may still be usable but are in one sense or another partially deficient.

Additionally, a data integrity hotline (1-800-736-9407) is maintained by NDSC.

SECTION 6.0

ACCOMMODATIONS AND ENVIRONMENTAL CONDITIONS

6.1 OVERVIEW

The laboratory is a 28,000 ft^2 secure laboratory facility with controlled access and designed to accommodate an efficient workflow and to provide a safe and comfortable work environment for employees. All visitors sign in and are escorted by laboratory personnel. Access is controlled by various measures.

The laboratory is equipped with structural safety features. Each employee is familiar with the location, use, and capabilities of general and specialized safety features associated with their workplace. The laboratory provides and requires the use of protective equipment including safety glasses, protective clothing, gloves, etc. OSHA and other regulatory agency guidelines regarding required amounts of bench and fume hood space, lighting, ventilation (temperature and humidity controlled), access, and safety equipment are met or exceeded.

Traffic flow through sample preparation and analysis areas is minimized to reduce the likelihood of contamination. Adequate floor space and bench top area is provided to allow unencumbered sample preparation and analysis space. Sufficient space is also provided for storage of reagents and media, glassware, and portable equipment. Ample space is also provided for refrigerated sample storage before analysis and archival storage of samples after analysis. Laboratory HVAC and deionized water systems are designed to minimize potential trace contaminants.

The laboratory is separated into specific areas for sample receiving, sample storage, sample disposal, organic glassware cleaning, inorganic glassware cleaning, organic sample preparation, metals sample preparation, GC Volatiles sample analysis, GC/MS Volatile sample analysis and GC Semi-volatile sample analysis, GC/MS Semi-volatile sample analysis, General Chemistry sample analysis, Metals sample analysis, and administrative functions.

6.2 ENVIRONMENT

Laboratory accommodation, test areas, energy sources, lighting are adequate to facilitate proper performance of tests. The facility is equipped with heating, ventilation, and air conditioning (HVAC) systems appropriate to the needs of environmental testing performed at this laboratory.

The environment in which these activities are undertaken does not invalidate the results or adversely affect the required accuracy of any measurements.

The laboratory provides for the effective monitoring, control and recording of environmental conditions that may affect the results of environmental tests as required by the relevant specifications, methods, and procedures. Such environmental conditions include humidity, voltage and temperature in the laboratory

When any of the method or regulatory required environmental conditions change to a point where they may adversely affect test results, analytical testing will be discontinued until the environmental conditions are returned to the required levels.

Environmental conditions of the facility housing the computer network and TALs are regulated to protect against raw data loss.

When the laboratory performs laboratory activities at sites or facilities outside its permanent control, it shall ensure that the requirements related to facilities and environmental conditions of this document are met.

Specific requirements for facility and environmental conditions, as well as periodic monitoring of conditions, are given in the Environmental Health & Safety Manual plus each laboratory's Facility Addendum.

6.3 WORK AREAS

There is effective separation between neighboring areas when the activities therein are incompatible with each other. Examples include:

- Volatile organic chemical handling areas, including sample preparation and waste disposal, and volatile organic chemical analysis areas.

Access to and use of all areas affecting the quality of analytical testing is defined and controlled by secure access to the laboratory building as described below in the Building Security section.

Adequate measures are taken to ensure good housekeeping in the laboratory and to ensure that any contamination does not adversely affect data quality. These measures include regular cleaning to control dirt and dust within the laboratory.

Work areas are available to ensure an unencumbered work area. Work areas include:

- Access and entryways to the laboratory.
- Sample receipt areas.
- Sample storage areas.
- Chemical and waste storage areas.
- Data handling and storage areas.
- Sample processing areas.
- Sample analysis areas.

6.4 RESPONDING TO EMERGENCIES

Employees must be aware of procedures to respond to all emergencies that might occur in the workplace. Employees must be familiar with the location and proper operation of all emergency equipment, evacuation routes and designated assembly areas for all areas where they work. Refer to the NDSC EH&S Manual Document No. NDSC-US EHS-QP46060. Sec. 7 and the laboratory's local EH&S Manual Addendum (UP-FM-002) for complete details. These documents provide direction for situations where normal operations of the laboratory are not possible (e.g., electrical failures, heating/air conditioning failures, fire/building evacuation, computer failures, hazardous material spills, injury to employees, pandemic flu, disruption of phone service, etc.)

In the event that the building or information technology (IT) systems would be severely challenged a designated disaster recovery team, which includes Facility Management, Maintenance, Safety, Laboratory/Executive Management, Public Relations, IT, QA and other applicable personnel depending on the scope of the disaster, would assemble at a designated area to assess the situation and formulate a plan.

6.5 BUILDING SECURITY

The laboratory is considered a secure facility. All outside doors are locked during normal business hours to prevent unauthorized entry. Building keys and alarm codes are distributed to employees as necessary. Employees are issued a building key card to access the facility.

All visitors to the laboratory must sign in and out in a visitor's logbook that is located in the lobby. A visitor is defined as any person who visits the laboratory who is not an employee of the laboratory. Both visitors and vendors must review and sign specific EH&S forms; and are escorted by laboratory personnel at all times, or the location of the visitor is noted in the visitor's logbook.

SECTION 7

QUALITY SYSTEM

7.1 QUALITY POLICY STATEMENT

The Quality Policy statement gives employees clear requirements for the production of analytical data. As an organization, all personnel are committed to high quality professional practice, testing and data, and service to our clients.

We strive to provide the highest quality data achievable by:

- Reading and understanding all of the quality documents applicable to each position and implementing the process in our work.
- Following all recordkeeping requirements; describing clearly and accurately all activities performed; recording "real time" as the task is carried out; understanding that it is never acceptable to "back date" entries and should additional information be required at a later date, the actual date and by whom the notation is made must be documented.
- Ensuring data integrity through the completeness, consistency, impartiality and accuracy of the data generated. Data is attributable, legible, contemporaneously recorded, original or a true copy, and accurate (ALCOA). This applies to manual paper documentation and electronic records.
- Providing accountability and traceability for each sample analyzed through proper sample handling, labeling, preparation, instrument calibration/qualification/validation, analysis, and reporting; establishing an audit trail (the who, what, when, and why) that identifies date, time, analyst, instrument used, instrument conditions, quality control samples (where appropriate and/or required by the method), and associated standard material.
- Emphasizing a total quality management process which provides impartiality, accuracy, and strict compliance with agency regulations and client requirements, giving the highest degree of confidence; understanding that meeting the requirements of the next employee in the work flow process is just as important as meeting the needs of the external client.
- Providing thorough documentation and explanation to qualify reported data that may not meet all requirements and specifications, but is still of use to the client; understanding this occurs only after discussion with the client on the data limitations and acceptability of this approach.
- Responding immediately to indications of questionable data, out-of-specification occurrences, equipment malfunctions, and other types of laboratory problems, with investigation and applicable corrective action; documenting these activities completely, including the reasons for the decisions made.
- Providing a work environment that ensures accessibility to all levels of management and encourages questions and expression of concerns on quality issues to management. Eurofins recognizes that the implementation of a quality assurance program requires management's commitment and support as well as the involvement of the entire staff
- Continually improve systems and manage risk to support quality improvement efforts in laboratory, administrative and managerial activities
- To comply with the ISO/IEC 17025:2005 and 2017 International Standard, the 2016 TNI Standard and to continually improve the effectiveness of the management system.

7.2 ETHICS AND DATA INTEGRITY

Eurofins Environment Testing is committed to ensuring the integrity of its data and meeting the quality needs of its clients. The laboratory operates our Ethics and Data Integrity program under the guidance of Eurofin's Key Guidance Document (KGD). The elements of our program include:

- An Ethics Policy (NDSC Document No. SOP01-ETHC-QP5252) and Employee Ethics Statements.
- Ethics and Compliance Officer (ECOs).
- A Training Program.
- Self-governance through disciplinary action for violations.
- A confidential mechanism for anonymously reporting alleged misconduct and a means for conducting internal investigations of all alleged misconduct. (NDSC Document No. ETHC-SOP38228
- Procedures and guidance for recalling data if necessary (NDSC Document No. NDSC-CAR-SOP38229).
- Effective external and internal monitoring system that includes procedures for internal audits (Section 17).
- Produce results, which are accurate and include QA/QC information that meets client pre-defined Data Quality Objective (DQO's).
- Present services in a confidential, honest and forthright manner.
- Provide employees with guidelines and an understanding of the Ethical and Quality Standards of our Industry.
- Provide procedures and guidance to ensure the impartiality and confidentiality of all data and customer information.
- Operate our facilities in a manner that protects the environment and the health and safety of employees and the public.
- Obey all pertinent federal, state and local laws and regulations and encourage other members of our industry to do the same.
- Educate clients as to the extent and kinds of services available.
- Assert competency only for work for which adequate personnel and equipment are available and for which adequate preparation has been made.
- Promote the status of environmental laboratories, their employees, and the value of services rendered by them.

7.3 QUALITY SYSTEM SUPPORTING DOCUMENTATION

The laboratory's Quality System is communicated through a variety of documents.

- Quality Assurance Manual – Each laboratory has a lab-specific QA manual.
- NDSC Official Documents – Each laboratory may use the Guidance (instructional use) documents at their discretion. Template documents are process documents that the laboratory's need to implement locally by using the document as is or as an outline to define their internal practices that meet the minimum requirements of the template. Required documents need to be implemented as is and listed in the laboratory's document control list.
- Key Guidance Documents (KGDs) - Documents compiled at the Group Service Centre (GSC) level by Functional Leaders (document owners) aimed at providing specific Eurofins groups of employees with guidelines necessary for the good conduct of their respective work.
- Laboratory SOPs – General and Technical

- Work Instructions - A subset of procedural steps, tasks or forms associated with an operation of a management system (e.g., checklists, preformatted bench sheets, forms).

7.3.1 Order of Precedence

In the event of a conflict or discrepancy between policies, the order of precedence is as follows:

- Quality Management Plan (QMP)
- NDSC Guidance Documents
- KGDs
- Laboratory QA/QC Policy Memorandum
- Laboratory Quality Assurance Manual (QA Manual)
- Laboratory SOPs and Policies
- Other (Work Instructions (WI), memos, flow charts, etc.)

Note: The laboratory has the responsibility and authority to operate in compliance with regulatory requirements of the jurisdiction in which the work is performed. Where the QMP requirement conflicts with those regulatory requirements, the regulatory requirements of the jurisdiction shall hold primacy. The laboratory's QA Manual shall take precedence over the QMP in those cases.

7.4 QA/QC OBJECTIVES FOR THE MEASUREMENT OF DATA

Quality Assurance (QA) is responsible for developing planned activities whose purpose is to provide assurance to all levels of management that a quality program is in place within the laboratory, and that it is functioning in an effective manner that is consistent with the requirements of NELAP, ISO 17025, and any other regulatory agencies (i.e., states) in which the laboratory maintains accreditation.

Quality Control is generally understood to be limited to the analyses of samples and to be synonymous with the term *"analytical quality control"*. QC refers to the routine application of statistically based procedures to evaluate and control the accuracy of results from analytical measurements. The QC program includes procedures for estimating and controlling precision and bias and for determining reporting limits.

Request for Proposals (RFPs) and Quality Assurance Project Plans (QAPP) provide a mechanism for the client and the laboratory to discuss the data quality objectives in order to ensure that analytical services closely correspond to client needs. In order to ensure the ability of the laboratory to meet the Data Quality Objectives (DQOs) specified in the QAPP, clients are advised to allow time for the laboratory to review the QAPP before being finalized. The client is responsible for developing the QAPP; however, the laboratory will provide support to the client for developing the sections of the QAPP that concern laboratory activities.

Historically, laboratories have described their QC objectives in terms of precision, accuracy, representativeness, comparability, completeness, selectivity and sensitivity (PARCCSS). Each laboratory SOP defines the required QC indicators.

7.4.1 Precision

The objective is to meet the performance for precision demonstrated for the methods on similar samples and to meet DQOs of the EPA and/or other regulatory programs. Precision is defined as the degree of reproducibility of measurements under a given set of analytical conditions (exclusive of field sampling variability). Precision is documented on the basis of replicate analysis, usually duplicate or matrix spike (MS) duplicate samples. The calculation of precision is described in Section 24.5.2.

7.4.2 Accuracy

The objective is to meet the performance for accuracy demonstrated for the methods on similar samples and to meet DQOs of the EPA and/or other regulatory programs. Accuracy is defined as the degree of bias in a measurement system. Accuracy may be documented through the use of laboratory control samples (LCS) and/or MS. A statement of accuracy is expressed as an interval of acceptance recovery about the mean recovery. The calculation of accuracy is described in Section 24.4.1.6.

7.4.3 Representativeness

The objective is to provide data which is representative of the sampled medium. Representativeness is defined as the degree to which data represent a characteristic of a population or set of samples and is a measurement of both analytical and field sampling precision. The representativeness of the analytical data is a function of the procedures used in procuring and processing the samples. The representativeness can be documented by the relative percent difference between separately procured, but otherwise identical samples or sample aliquots.

The representativeness of the data from the sampling sites depends on both the sampling procedures and the analytical procedures. Refer to the laboratory SOPs for subsampling and homogenization techniques appropriate to the analytical method.

7.4.3 Comparability

The objective is to provide analytical data for which the accuracy, precision, representativeness and reporting limit statistics are similar to these quality indicators generated by other laboratories for similar samples, and data generated by the laboratory over time.

Comparability is documented by inter-laboratory studies carried out by regulatory agencies or carried out for specific projects or contracts, by comparison of periodically generated statements of accuracy, precision and reporting limits with those of other laboratories.

7.4.5 Completeness

The completeness objective for data is 90% (or as specified by a particular project), expressed as the ratio of the valid data to the total data over the course of the project. Data will be considered valid if they are adequate for their intended use. Data usability will be defined in a QAPP, project scope or regulatory requirement. Data validation is the process for reviewing data to determine its usability and completeness. If the completeness objective is not met, actions will be taken internally and with the data user to improve performance. This may take the form of an audit to evaluate the methodology and procedures as possible sources for the difficulty or may result in a recommendation to use a different method.

7.4.6 Selectivity

Selectivity is defined as: The capability of a test method or instrument to respond to a target substance or constituent in the presence of non-target substances. Target analytes are separated from non-target constituents and subsequently identified/detected through one or more of the following, depending on the analytical method: extractions (separation), digestions (separation), inter-element corrections (separation), use of matrix modifiers (separation), specific retention times (separation and identification), confirmations with different columns or detectors (separation and identification), specific wavelengths (identification), specific mass spectra (identification) and specific electrodes (separation and identification).

7.4.7 Sensitivity

Sensitivity refers to the amount of analyte necessary to produce a detector response that can be reliably detected above the Method Detection Limit (MDL) or Limit of Detection (LOD) or quantified above the Reporting Limit (RL) or Limit of Quantitation (LOQ).

7.5 CRITERIA FOR QUALITY INDICATORS

The laboratory maintains tables, housed in TALS that contains tables that summarize the precision and accuracy acceptability limits for performed analyses. This summary includes an effective date, is updated each time new limits are generated and is managed by the laboratory's QA department. Limits are archived within the LIMS when replaced. Unless otherwise noted, limits within these tables are laboratory generated. Some acceptability limits are derived from US EPA methods when they are required. Where US EPA method limits are not required, the laboratory has developed limits from evaluation of data from similar matrices. Criteria for the development of control limits are contained in Section 24.6.

7.6 STATISTICAL QUALITY CONTROL

Statistically-derived precision and accuracy limits are required by selected methods (such as SW-846). The laboratory routinely utilizes statistically-derived limits to evaluate method performance and determine when corrective action is appropriate. The analysts use the current limits entered into TALs. The Quality Assurance department maintains an archive of all limits used within the laboratory. These limits are maintained in TALS as part of the analytical historical record. If a method defines the QC limits, the method limits are used.

If a method requires the generation of historical limits, the lab develops such limits from recent data in the QC database of the TALs following the guidelines described in Section 24.6. All calculations and limits are documented and dated when approved and effective. On occasion, a client requests contract-specified limits for a specific project.

Current QC limits are entered and maintained in the TALs analyte database. As sample results and the related QC are entered into TALs, the sample QC values are compared with the limits in TALs to determine if they are within the acceptable range. The analyst then evaluates if the sample needs to be rerun or re-extracted/rerun or if a comment should be added to the report explaining the reason for the QC outlier.

7.6.1 QC Charts

Statistical control limits and control charts are used to establish method performance of a given analysis and to monitor trends of QC results graphically over time. Once a data base of the laboratory results for a method/matrix/QC analyte combination is established, the acceptability of a given analysis of that QC parameter (and of the analytical batch to which it belongs) can be evaluated in light of the laboratory's normal performance. This is intended to help identify problems before they might affect data. Often, patterns of response that are not at all evident in sets of numbers are very distinct when the same values are viewed as a chronological graph.

The charting program in the TALs system at Eurofins Chicago automatically applies an outlier test to the queried data and identifies the data points that fail the test. The program also has 'Warning Triggers' for each of the chart types that are set as follows:
"Warn if number of consecutive points outside warning limit" (currently set at 3 points).
"Warn if number of consecutive points on either side of mean" (currently set at 5 points).

Establishment of Limits

The purpose of using statistical control limits is to define, for each analyte in a given method/matrix/QC type combination, a range of expected values. This range encompasses the random variation that occurs normally in the laboratory and allows one to evaluate control samples in that context, rather than according to an arbitrary or external set of values. Limits for accuracy and precision are defined below:

Accuracy

As recoveries of a QC analyte in a given matrix are tabulated over time, a mean value for recovery is established, as is the standard deviation (s) of those recoveries. If the analysis is in statistical control (e.g., if the set of QC recoveries over time show random variation about the mean) approximately 99.7% of all recoveries for that QC will fall within three standard deviations (3s) of the mean. Thus, assuming that the mean itself is an acceptable level of recovery, the values corresponding to 3s above and 3s below the mean are defined as the Control Limits. Any single recovery outside these values is assumed to have resulted from some circumstance other than normal variation and shall be investigated.

Roughly 95% of points should fall within 2s of the mean. The values +2s and -2s are the Warning Limits. Any normal result has approximately a 1/20 chance of being between 2s and 3s from the mean, so a result in this region doesn't necessarily warrant corrective action, but attention should be paid to such points.

Precision

Precision is used to indicate matrix variability so that appropriate decisions can be made by the client when repeated analyses vary significantly. The coefficient of variation, expressed as a percentage (e.g., the %RSD) for the data set used to calculate accuracy control limits defines the control limit for precision. Duplicate analyses of the QC samples, such as duplicates or MS/MSD, should have an RPD less than or equal to this established precision control limit to be considered free of matrix interferences.

The laboratory calculates statistical control limits on an annual basis or more frequently if instrument conditions or method procedure warrants the re-calculation of control limits. The QA Manager and Department Managers/Supervisors are responsible for the review and approval of the limits for use.

7.7 QUALITY SYSTEM METRICS

In addition to the QC parameters discussed above, the entire Quality System is evaluated on a monthly basis through the use of specific metrics (refer to Section 18). These metrics are used to drive continuous improvement in the laboratory's Quality System.

SECTION 8

DOCUMENT CONTROL

8.1 OVERVIEW

The QA Department is responsible for the control of documents used in the laboratory to ensure that approved, up-to-date documents are in circulation and out-of-date (obsolete) documents are archived or destroyed. The following documents, at a minimum, must be controlled:

- Laboratory Quality Assurance Manual (QAM)
- Laboratory Standard Operating Procedures (SOP)
- Laboratory Policies

- Work Instructions and Forms
- NDSC Documents[1]
- KGDs[1]

[1]Includes locally implemented documents that are document controlled within the laboratory's document control system.

The NDSC and/or KGD documents are only considered controlled when they are read on the intranet site. Printed copies are considered uncontrolled unless the laboratory physically distributes them as controlled documents. A detailed description of the procedure for issuing, authorizing, controlling, distributing, and archiving NDSC Official Documents is found in Document No. CED-Q-DC-SOP45894, NDSC Document Control and Archiving. KGD documents are controlled according to the laboratory's internal document control procedure is defined in the laboratory SOP *UP-QA-042*, Signature Authority & Document Control.

The laboratory QA Department also maintains access to various references and document sources integral to the operation of the laboratory. This includes reference methods and regulations. Instrument manuals (hard or electronic copies) are also maintained by the laboratory.

The laboratory maintains control of records for raw analytical data and supporting records such as audit reports and responses, logbooks, standard logs, training files, MDL studies, Proficiency Testing (PT) studies, certifications and related correspondence, and corrective action reports. Raw analytical data consists of bound logbooks, instrument printouts, any other notes, magnetic media, electronic data and final reports. Discussion on records control is described in Section 16.

8.2 DOCUMENT APPROVAL AND ISSUE

The pertinent elements of the document control system includes a unique document title and number, pagination, the total number of pages of the item or an 'end of document' page, the effective date, revision number and the laboratory's name. The Quality Assurance personnel are responsible for the maintenance of this system.

Controlled documents are authorized by the QA Department. In order to develop a new document, the responsible manager submits an electronic draft copy to the QA Department for review and approval before use. Once approved, the document is issued a document control number and is added to the tracking spreadsheet located on the LAN at \\tacorp\Corp\QA\QA_Facilities\Chicago-QA\Document-Management\Lists\CHI_SOP List.xls. Upon approval, QA personnel add the identifying version information to the document and retain that document as the official document on file. That document is then provided to all applicable operational units. Controlled documents are identified as such and records of their distribution are kept by the QA Department. Document control may be achieved by either electronic or hardcopy distribution.

The QA Department maintains a list of the official versions of controlled documents.

Quality System Policies and Procedures will be reviewed at a minimum of every two years, or more often as required and revised as appropriate. Changes to documents occur when a procedural change warrants a revision of the document.

8.3 PROCEDURES FOR DOCUMENT CONTROL POLICY

For changes to the QA Manual, refer to laboratory SOP *UP-QA-032*, SOP Change Protocol. Uncontrolled copies must not be used within the laboratory. Previous revisions and back-up data are stored by the QA department. Hardcopies are filed within the QA department or in are

archived in the secure data storage room and electronic copies are stored on the LAN in the \\tacorp\Corp\QA\QA_Facilities\Chicago-QA\Document-Management\SOPs then in individual department directories for the applicable revision.

For changes to SOPs, refer to the NDSC Document No. *CED-Q_DC_SOP45969*, Writing a Standard Operating Procedure and the laboratory SOP *UP-QA-042*. The SOPs identified above also defines the process of changes to SOPs.

Forms, worksheets, work instructions and information are organized by department in the QA office and tracked on the LAN in the \\tacorp\Corp\QA\QA_Facilities\Chicago-QA\Document-Management\Lists\CHI_SOP List excel spreadsheet. Electronic versions are kept on the LAN in the appropriate directory; hard copies are kept in QA files. The procedure for the care of these documents is in the laboratory SOP *UP-QA-042*, Signature Authority & Document Control.

8.4 OBSOLETE DOCUMENTS

All invalid or obsolete documents are removed, or otherwise prevented from unintended use. The laboratory has specific procedures as described above to accomplish this. In general, obsolete documents are collected from employees according to distribution lists and are marked obsolete on the cover or destroyed. At least one copy of the obsolete document is archived as described in Section 16 and according to SOP *UP-DM-001*, Process Operation & Record Retention & Purging.

SECTION 9

SERVICE TO THE CLIENT

9.1 OVERVIEW

The laboratory has established procedures for the review of work requests and contracts, oral or written. The procedures include evaluation of the laboratory's capability and resources to meet the contract's requirements within the requested time period. All requirements, including the methods to be used, must be adequately defined, documented and understood. For many environmental sampling and analysis programs, testing design is site or program specific and does not necessarily fit into a standard laboratory service or product. It is the laboratory's intent to provide both standard and customized environmental laboratory services to our clients.

A thorough review of technical and QC requirements contained in contracts is performed to ensure project success. The appropriateness of requested methods, and the lab's capability to perform them must be established. Projects, proposals and contracts are reviewed for adequately defined requirements and the laboratory's capability to meet those requirements. Alternate test methods that are capable of meeting the clients' requirements may be proposed by the lab. A review of the lab's capability to analyze non-routine analytes is also part of this review process.

All projects, proposals and contracts are reviewed for the client's requirements in terms of compound lists, test methodology requested, sensitivity (detection and reporting levels), accuracy, and precision requirements (% Recovery and RPD). The reviewer ensures that the laboratory's test methods are suitable to achieve these requirements and that the laboratory holds the appropriate certifications and approvals to perform the work. The laboratory and any potential subcontract laboratories must be certified, as required, for all proposed tests.

Electronic or hard copy deliverable requirements are evaluated against the laboratory's capacity for production of the documentation.

If the laboratory cannot provide all services but intends to subcontract such services, whether to another Eurofins facility or to an outside firm, this will be documented and discussed with the client prior to contract approval. (Refer to Section 10 for Subcontracting Procedures.)

The laboratory informs the client of the results of the review if it indicates any potential conflict, deficiency, lack of accreditation, or inability of the lab to complete the work satisfactorily. Any discrepancy between the client's requirements and the laboratory's capability to meet those requirements is resolved in writing before acceptance of the contract. It is necessary that the contract be acceptable to both the laboratory and the client. Amendments initiated by the client and/or Eurofins Chicago, are documented in writing.

All contracts, QAPPs, Sampling and Analysis Plans (SAPs), contract amendments, and documented communications become part of the project record.

The same contract review process used for the initial review is repeated when there are amendments to the original contract by the client, and the participating personnel are informed of the changes.

9.2 REVIEW SEQUENCE AND KEY PERSONNEL

Appropriate personnel will review the work request at each stage of evaluation.

For routine projects and other simple tasks, a review by the Project Manager (PM) is considered adequate. The PM confirms that the laboratory has any required certifications, that it can meet the clients' data quality and reporting requirements and that the lab has the capacity to meet the clients turn around needs. It is recommended that, where there is a sales person assigned to the account, an attempt should be made to contact that sales person to inform them of the incoming samples.

For new, complex or large projects, the proposed contract is given to the National Account Director, who will decide which lab will receive the work based on the scope of work and other requirements, including certification, testing methodology, and available capacity to perform the work. The contract review process is outlined in NDSC Document No. *CA-L-P-002, Contract Compliance Policy*.

This review encompasses all facets of the operation. The scope of work is distributed to the appropriate personnel, as needed based on scope of contract, to evaluate all of the requirements shown above (not necessarily in the order below):

- Contract Administrator
- Laboratory Project Manager
- Laboratory Director and/or Technical Director
- Account Executives
- Quality Managers
- Laboratory Environmental Health and Safety Managers/Directors

The Laboratory Director reviews the formal laboratory quote and makes final acceptance for their facility.

The Sales Director, Contract Administrator, Account Executive or Proposal Coordinator then submits the final proposal to the client.

In the event that one of the above personnel is not available to review the contract, his or her back-up will fulfill the review requirements.

9.3 Balancing Laboratory Capacity and Workload

Evaluating laboratory capacity to perform specific projects is the responsibility of the Laboratory Directors and Managers, and the Client Services director and manager. Many analysts are cross-trained to perform a variety of tests, and there is redundant equipment available in case of malfunctions. This minimizes the need to evaluate small and medium size projects against capacity available to complete them. Large and complex projects are reviewed against capacity estimates before bids are submitted to ensure that the client's analysis schedule is met. Regularly scheduled meetings are held between laboratory management, PMs, Client Services and QA personnel to review progress with current projects, as well as special requirements of new work scheduled for the laboratory. Laboratory capacity and backlog is tracked on a continuous basis using information from the Laboratory Sample Information System (LIMS) including turnaround time, and work in-house.

9.4 DOCUMENTATION

The Contracts Department maintains copies of all signed contracts. The laboratory's Proposal Coordinator also maintains a copy.

Appropriate records are maintained for every contract or work request. All stages of the contract review process are documented and include records of any significant changes.

The contract will be distributed to and maintained by the appropriate sales/marketing personnel and the Regional Account Manager. A copy of the contract and formal quote will be filed with the laboratory PM, Lab Director or local account representative/proposal coordinator.

Records are maintained of pertinent discussions with a client relating to the client's requirements or the results of the work during the period of execution of the contract. The PM keeps a phone log of conversations with the client.

9.4.1 Project-Specific Quality Planning

Communication of contract specific technical and QC criteria is an essential activity in ensuring the success of site specific testing programs. To achieve this goal, the laboratory assigns a PM to each client. The PM is the first point of contact for the client. It is the PM's responsibility to ensure that project specific technical and QC requirements are effectively evaluated and communicated to the laboratory personnel before and during the project. QA department involvement may be needed to assist in the evaluation of custom QC requirements.

PM's are the primary client contact and they ensure resources are available to meet project requirements, they coordinate opportunities and work with laboratory management and supervisory staff to ensure that resources are sufficient to perform work for the client's project.

Prior to work on a new project, the dissemination of project information and/or project opening meetings may occur to discuss schedules and unique aspects of the project. Items to be discussed may include the project technical profile, turnaround times, holding times, methods, analyte lists, reporting limits, deliverables, sample hazards, or other special requirements. The PM introduces new project information to maximize production and client satisfaction, while maintaining quality. Project notes may be associated with each sample batch as a reminder upon sample receipt and analytical processing.

Any change that may occur within an active project is agreed upon between the client/regulatory agency and the PM/laboratory. These changes (e.g., use of a non-standard method or modification of a method) and approvals must be documented prior to implementation.

Documentation pertains to any document, e.g., letter, e-mail, variance, contract addendum, which has been signed by both parties.

Such changes are also communicated to the laboratory during production meetings and through updated project notes. The laboratory staff is then introduced to the modified requirements via the PM or the individual laboratory Technical Managers. After the modification is implemented into the laboratory process, documentation of the modification is retained as an attached document to the project or job in LIMS or as an NCM in the LIMS system which can then be added to the case narrative of the data report(s).

The laboratory strongly encourages client visits to the laboratory and for formal/informal information sharing session with employees in order to effectively communicate ongoing client needs as well as project specific details for customized testing programs.

9.5 SPECIAL SERVICES

The laboratory cooperates with clients and their representatives to monitor the laboratory's performance in relation to work performed for the client. It is the laboratory's goal to meet all client requirements in addition to statutory and regulatory requirements. The laboratory has procedures to ensure confidentiality to clients (Section 17 and 25)

The laboratory's standard procedures for reporting data are described in Section 25. Special services are also available and provided upon request. These services include:

- Reasonable access for our clients or their representatives to the relevant areas of the laboratory for the witnessing of tests performed for the client.
- Assist client specified third party data validators as specified in the client's contract.
- Supplemental information pertaining to the analysis of their samples. Note: An additional charge may apply for additional data/information that was not requested prior to the time of sample analysis or previously agreed upon.

When the client requests a statement of conformity to a specification or standard based on the analysis performed by the laboratory (e.g., pass/fail, in-tolerance/out-of-tolerance), the decision rule shall be clearly defined. Unless inherent in the requested specification or standard, the decision rule selected shall be communicated to the client. Associated reporting requirements are addressed in Section 25.2.18.

9.6 CLIENT COMMUNICATION

PMs are the primary communication link to the clients. They shall inform their clients of any delays in project completion as well as any con-conformances in either sample receipt or sample analysis. Project management will maintain ongoing client communication throughout the entire client project.

Technical Managers are available to discuss any technical questions or concerns that the client may have.

9.7 Reporting

The laboratory works with our clients to produce any special communication reports required by the contract.

9.8 Client Feedback and Surveys

The laboratory assesses both positive and negative client feedback. The results are used to improve overall laboratory quality and client services. Eurofins Sales and Marketing teams periodically develop lab and client specific surveys to assess client satisfaction.

Eurofins Client Advocacy team has developed a lab/client specific survey to assess client satisfaction. With each report emailed to a client, a link to a Report/Project Feedback Survey is attached with the invitation to the client to provide feedback regarding the service they have received.

When a complaint is received, we determine, to the best of our ability, the extent of the issue and what data is in question. The person receiving the complaint documents this information and promptly forwards it to the appropriate management personnel where the work in question was performed. If a data reporting error is discovered, the final report and/or data must be regenerated with the correct value(s).

The QA Manager is responsible for entering client concerns into the Complaint Data Base. In some cases, a CAR (Investigation and Corrective Action Report) is initiated to address and document the situation. While an individual issue may not warrant a formal investigation, QA monitors these issues for potential trends and will open an investigation/CAR is a trend is evident.

SECTION 10

SUBCONTRACTING OF TESTS

10.1 OVERVIEW

For the purpose of this quality manual, the phrase subcontract laboratory refers to a laboratory external to the Eurofins Chicago laboratory. The phrase “work sharing” refers to internal transfers of samples between the Eurofins Chicago laboratory. The term outsourcing refers to the act of subcontracting tests.

When contracting with our clients, the laboratory makes commitments regarding the services to be performed and the data quality for the results to be generated. When the need arises to outsource testing for our clients because project scope, changes in laboratory capabilities, capacity or unforeseen circumstances, we must be assured that the subcontractors or work sharing laboratories understand the requirements and will meet the same commitments we have made to the client. Refer to NDSC Documents on Subcontracting (NDSC-US-SUB-SOP44936).

When outsourcing analytical services, the laboratory will assure, to the extent necessary, that the subcontract or work sharing laboratory maintains a program consistent with the requirements of this document, the requirements specified in TNI / ISO 17025 and/or the client’s Quality Assurance Project Plan (QAPP). All QC guidelines specific to the client’s analytical program are transmitted to the subcontractor and agreed upon before sending the samples to the subcontract facility. Additionally, work requiring accreditation will be placed with an appropriately accredited laboratory. The laboratory performing the subcontracted work will be identified in the final report, as will non-TNI accredited work where required.

PMs or other responsible Client Service members, for the Export Lab (i.e. the Eurofins Chicago laboratory that transfers samples to another laboratory) are responsible for obtaining client approval prior to subcontracting any samples. The laboratory will advise the client of a subcontract or work sharing arrangement in writing and when possible approval from the client

shall be obtained and retained in the project folder. Standard Eurofins Chicago Terms & Conditions include the flexibility to subcontract samples within the Eurofins laboratories network. Therefore, additional advance notification to clients for intra-laboratory subcontracting is not necessary unless specifically required by a client contract.

Note: In addition to the client, some regulating agencies (e.g., USDA) or contracts (e.g., certain USACE projects), may require notification prior to placing such work.

10.2 QUALIFYING AND MONITORING SUBCONTRACTORS

Whenever a PM [or Account Executive (AE) or Client Relationship Manager, etc.] becomes aware of a client requirement or laboratory need where samples must be outsourced to another laboratory, the other laboratory(s) shall be selected based on the following:

- Subcontractors specified by the client - In these circumstances, the client assumes responsibility for the quality of the data generated from the use of a subcontractor.
- Subcontractors reviewed by Eurofins Chicago – Firms which have been reviewed by the company and are known to meet standards for accreditations (e.g., State, TNI and DoD/DOE); technical specifications; legal and financial information.

A listing of vendors is available on the Eurofins intranet site.

All Eurofins laboratories are pre-qualified for work sharing provided they hold the appropriate accreditations and can adhere to the project/program requirements. Client approval is not necessary unless specifically required by the contract. In these cases, the client must provide acknowledgement that the samples can be sent to that facility (an e-mail is sufficient documentation or if acknowledgement is verbal, the date, time, and name of person providing acknowledgement must be documented). The originating laboratory is responsible for communicating all technical, quality, and deliverable requirements as well as other contract needs.

10.2.1 When the potential sub-contract laboratory has not been previously approved, Account Executives or PMs may nominate a laboratory as a subcontractor based on need. The decision to nominate a laboratory must be approved by the Client Relations Manager (CRM) or Laboratory Director. The Client Relations Manager (CRM) or Laboratory Director requests that the QA Manager or PM begin the process of approving the subcontract laboratory. Refer to the NDSC Document No. NDSC US-SUB-SOP44936, Subcontracting Procedures.

Once the appropriate accreditation and legal information is received by the laboratory, it is evaluated for acceptability (where applicable) and forwarded to the NDSC Quality Information Manager (QIM) for review. After the NDSC QIM reviews the documents for completeness, the information is forwarded to the Finance Department for formal signature and contracting with the laboratory. The approved vendor will be added to the approved subcontractor list on the intranet site and the finance group is concurrently notified.

The client will assume responsibility for the quality of the data generated from the use of a subcontractor they have requested the lab to use. The qualified subcontractors on the intranet site are known to meet minimal standards. Eurofins Chicago does not certify laboratories. The subcontractors on our approved list can only be recommended to the extent that we would use them.

10.3 Oversight and Reporting

10.3.1 The status and performance of qualified subcontractors will be monitored by the

NDSC, and includes an annual review process (see NDSC Document No. NDSC-US-SUB-SOP44936). Any problems identified will be brought to the attention of NDSC Procurement personnel.

- Complaints shall be investigated. Documentation of the complaint, investigation and corrective action will be maintained in the subcontractor's file on the intranet site. Complaints are posted using the Vendor Performance Report.
- Information shall be updated on the intranet when new information is received from the subcontracted laboratories.
- Subcontractors in good standing will be retained on the intranet listing. CSO personnel will notify all Eurofins laboratories, NDSC and Corporate Contracts if any laboratory requires removal from the intranet site. This notification will be posted on the intranet site and e-mailed to all Client Service Personnel, Laboratory Directors, QA Managers and Sales Personnel.

Prior to initially sending samples to the subcontracted laboratory, the PM confirms their certification status to determine if it's current and scope-inclusive. The information is documented within the project records.

The laboratory's certifications can be viewed on the company's website.

10.3.2 All subcontracted samples must be accompanied by a Eurofins Chicago Chain of Custody (COC). A copy of the original COC sent by the client must be available in TALS for all samples workshared within the Eurofins laboratory network. Client COCs are only forwarded to external subcontractors when samples are shipped directly from the project site to the subcontractor lab. Under routine circumstances, the client COCs are not provided to external subcontractors.

Through communication with the subcontracted laboratory, the PM monitors the status of the subcontracted analyses, facilitates successful execution of the work, and ensures the timeliness and completeness of the analytical report.

Non-TNI accredited work must be identified in the subcontractor's report as appropriate. If TNI accreditation is not required, the report does not need to include this information.

Reports submitted from subcontractor laboratories are not altered and are included in their original form in the final project report. This clearly identifies the data as being produced by a subcontractor facility. If subcontract laboratory data is incorporated into the laboratory's EDD (i.e., imported), the report must explicitly indicate which lab produced the data for which methods and samples.

Note: The results submitted by a Eurofins work sharing laboratory may be transferred electronically and the results reported by the Eurofins Chicago work sharing lab are identified on the final report. The report must explicitly indicate which lab produced the data for which methods and samples. The final report must include a copy of the completed COC for all work sharing reports.

10.4 CONTINGENCY PLANNING

The full qualification of a subcontractor may be waived to meet emergency needs. This decision & justification must be documented in the project files, and the 'Purchase Order Terms and Conditions for Subcontract Laboratory Services' must be sent with the samples and COC.

In the event this provision is utilized, the laboratory (e.g., PM) will be required to verify and document the applicable accreditations of the subcontractor. All other quality and accreditation requirements will still be applicable, but the subcontractor need not have signed a subcontract agreement with Eurofins Chicago at this time.

The use of any emergency subcontractor will require the PM to complete a New Vendor Add Form in order to process payment to the vendor and add them to LIMS. This form requires the user to define the subcontractor's category/s of testing and the reason for testing.

10.5 Use of NELAP and A2LA Logo

It is not laboratory policy to use these logos on any company letterhead, including analytical reports.

SECTION 11

PURCHASING SERVICES AND SUPPLIES

11.1 OVERVIEW

Evaluation and selection of suppliers and vendors is performed, in part, on the basis of the quality of their products, their ability to meet the demand for their products on a continuous and short term basis, the overall quality of their services, their past history, and competitive pricing. This is achieved through evaluation of objective evidence of quality furnished by the supplier, which can include certificates of analysis, recommendations, and proof of historical compliance with similar programs for other clients. To ensure that quality critical consumables and equipment conform to specified requirements, which may affect quality, all purchases from specific vendors are approved by a member of the supervisory or management staff.

Contracts will be signed in accordance with the Spending and Contracting Authority Matrix for US Environment available on EETNet. Request for Proposals (RFP's) will be issued where more information is required from the potential vendors than just price. Guidance on Procurement and Contracts Policy. RFP's allow the laboratory to determine if a vendor is capable of meeting requirements such as supplying all of the laboratory facilities, meeting required quality standards and adhering to necessary ethical and environmental standards. The RFP process also allows potential vendors to outline any additional capabilities they may offer.

11.2 GLASSWARE

Glassware used for volumetric measurements must be Class A or verified for accuracy according to laboratory procedure. Pyrex (or equivalent) glass should be used where possible. For safety purposes, thick-wall glassware should be used where available.

11.3 REAGENTS, STANDARDS & SUPPLIES

Purchasing guidelines for equipment and reagents must meet the requirements of the specific method and testing procedures for which they are being purchased. Solvents and acids are pre-tested in accordance with NDSC Document No. NDSC-QA-SOP46704, Acid and Solvent Lot Testing and Approval Program. Approval information for the solvents and acids tested under NDSC Document No. NDSC-QA-SOP46704 is stored on the Eurofins Environment Testing America intranet SharePoint, under Solvent Approvals. A master list of all tested materials, as well as the certificates of analysis for the materials, is stored in the same location.

11.3.1 Purchasing

Chemical reagents, solvents, glassware, and general supplies are ordered as needed to maintain sufficient quantities on hand. Materials used in the analytical process must be of a known quality. The wide variety of materials and reagents available makes it advisable to specify recommendations for the name, brand, and grade of materials to be used in any determination. This information is contained in the method SOP.

11.3.2 Receiving

It is the responsibility of the facility manager and sample login staff or designee to receive the shipment and document date received. It is the responsibility of the analyst who ordered the materials to date the material when opened for use and inspect the item. Once the ordered reagents or materials are received, the analyst reviews the information on the label or packaging to ensure that the purchase meets the quality level specified when ordered. This is documented through the addition of the received date and initials to the information on the daily order log.

The department manager or supervisor verifies the lot numbers of received solvents and acids against the pre-approved lists. If a received material is listed as unapproved, or is not listed, it is sequestered and returned to the vendor. Alternatively, the laboratory may test the material for the intended use, and if it is acceptable, document the approval on the approval list. Records of any testing performed locally are maintained on the shared “public” folder on the computer network.

Materials may not be released for use in the laboratory until they have been inspected, verified as suitable for use, and the inspection/verification has been documented.

Safety Data Sheets (SDSs) are available in the facility/safety manager’s office on file and online through the Company’s intranet website. Anyone may review these for relevant information on the safe handling and emergency precautions of on-site chemicals.

11.3.3 Specifications

Methods used in the laboratory specify the grade of reagent that must be used in the procedure. If the quality of the reagent is not specified, analytical reagent grade will be used. It is the responsibility of the analyst to check the procedure carefully for the suitability of grade of reagent.

Chemicals must not be used past the manufacturer’s expiration date and must not be used past the expiration time noted in a method SOP. If expiration dates are not provided, the laboratory may contact the manufacturer to determine an expiration date.

The laboratory assumes a five year expiration date on inorganic dry chemicals and solvents unless noted otherwise by the manufacturer or by the reference source method. Chemicals/solvents should not be used past the manufacturer’s or SOP expiration date unless ‘verified’ as outlined below.

- An expiration date cannot be extended if the dry chemical/solvent is discolored or appears otherwise physically degraded. In this case, the dry chemical/solvent must then be discarded.
- Expiration dates can be extended if the dry chemical/solvent is found to be satisfactory based on acceptable performance of quality control samples (Continuing Calibration Verification (CCV), Blanks, Laboratory Control Sample (LCS), etc.).

- If the dry chemical/solvent is used for the preparation of standards, the expiration dates can be extended 6 months if the dry chemical/solvent is compared to an unexpired independent source in performing the method and the performance of the dry chemical/solvent is found to be satisfactory. The comparison must show that the dry chemical/solvent meets CCV limits. The comparison studies are maintained on-file and available for review within the department where the study was performed.

Wherever possible, standards must be traceable to national or international standards of measurement or to national or international reference materials. Records to that effect are available to the user.

Compressed gases in use are checked for pressure and secure positioning daily. To prevent a tank from going to dryness, or introducing potential impurities, the pressure should be closely watched as it decreases to approximately 15% of the original reading, at which point it should be replaced. For example, a standard sized laboratory gas cylinder containing 3,000 psig of gas should be replaced when it drops to approximately 500 psig. The quality of the gases must meet method or manufacturer specification or be of a grade that does not cause any analytical interference.

Water used in the preparation of samples, standards or reagents must have a specific conductivity of less than 1- umho/cm (or specific resistivity of greater than 1.0 megaohm-cm) at 25°C. The specific conductivity is checked and recorded daily. If the water's specific conductivity is less than the specified limit, the Facility Manager and appropriate Department Managers/Supervisors must be notified immediately in order to notify all departments, decide on cessation (based on intended use) of activities, and make arrangements for correction.

The laboratory may purchase reagent grade (or other similar quality) water for use in the laboratory. This water must be certified clean by the supplier for all target analytes or otherwise verified by the laboratory prior to use. This verification is documented.

Standard lots are verified before first time use if the laboratory switches manufacturers or has historically had a problem with the type of standard.

Purchased bottleware used for sampling must be certified clean and the certificates must be maintained. If uncertified bottleware is purchased, all lots must be verified clean prior to use. This verification must be maintained.

Records of manufacturer's certification and traceability statements are maintained in files or binders in each laboratory section. These records include date of receipt, lot number (when applicable), and expiration date (when applicable). Incorporation of the item into the record indicates that the analyst has compared the new certificate with the previous one for the same purpose and that no difference is noted, unless approved and so documented by the Technical Director or QA Manager.

11.3.4 Storage

Reagent and chemical storage is important from the aspects of both integrity and safety. Light-sensitive reagents may be stored in brown-glass containers. Storage conditions are per the NDSC HSE Manual, Document No. NDSC-US EHS-QP46060, the local laboratory EH&S Manual Addendum (UP-FM-002) and method SOPs or the manufacturer's instructions. Table11-1 details specific storage instructions for reagents and chemicals. Section 21 discusses conditions for standard storage.

11.4 PURCHASE OF EQUIPMENT/INSTRUMENTS/SOFTWARE

When a new piece of equipment is needed, either for additional capacity or for replacing inoperable equipment, the analyst or supervisor makes a supply request to the Department Manager and/or the Laboratory Director. A decision is made as to which piece of equipment can best satisfy the requirements. The appropriate written requests are completed and purchasing places the order.

Upon receipt of a new or used piece of equipment, an identification name is assigned and added to the equipment list, described in Section 20. IT must also be notified so that they can synchronize the instrument for back-ups and or TALS import. Its capability is assessed to determine if it is adequate or not for the specific application. For instruments, a calibration curve is generated, followed by MDLs, Demonstration of Capabilities (DOCs), and other relevant criteria (refer to Section 19). For software, its operation must be deemed reliable and evidence of instrument verification must be retained by the IT Department or QA Department as specified in the laboratory's procedure for software verification. Software certificates supplied by the vendors are filed with the LIMs Administrator. The manufacturer's operation manual is retained in a designated area or near the instrument.

11.5 SERVICES

Service to analytical instruments (except analytical balances) is performed on an as needed basis. Routine preventative maintenance is discussed in Section 20. The need for service is determined by analysts and/or Technical Managers. The service providers that perform the services are approved by the Technical Manager/Laboratory Director.

Analytical balances are serviced and calibrated annually in accordance with SOP UP-QA-003, Balance Calibration Care and Use. Calibration and maintenance services are performed on-site, and the balances are returned to use immediately following successful calibration. Calibration certificates are filed for reference in the QA Department. If the calibration was unsuccessful, the balance is immediately removed from service and segregated pending either further maintenance or disposal.

Calibration services for support equipment such as thermometers, weight sets, autopipettors, etc., are obtained from vendors with current and valid ISO 17025 accreditation for calibration of the specific piece of equipment. Prior to utilizing the vendor's services, the vendor's accreditation status is verified. Once the equipment has been calibrated, the calibration certificates are reviewed by the QA department, and documentation of the review is filed with the calibration certificates. The equipment is then returned to service within the laboratory.

11.6 SUPPLIERS

Eurofins Environment Testing America selects vendors through a competitive proposal / bid process, strategic business alliances or negotiated vendor partnerships (contracts). The level of control used in the selection process is dependent on the anticipated spending amount and the potential impact on Eurofins Environment Testing America business. Vendors that provide test and measuring equipment, solvents, standards, certified containers, instrument related service contracts or subcontract laboratory services shall be subject to more rigorous controls than vendors that provide off-the-shelf items of defined quality that meet the end use requirements. The purchasing system includes all suppliers/vendors that have been approved for use.

Evaluation of suppliers is accomplished by ensuring the supplier ships the product or material ordered and that the material is of the appropriate quality. This is documented by signing off on

packing slips or other supply receipt documents. The purchasing documents contain the data that adequately describe the services and supplies ordered.

Any issues of vendor performance are to be reported immediately by the laboratory staff to the Corporate Purchasing Group and laboratory QA.

The Purchasing Group will work through the appropriate channels to gather the information required to clearly identify the problem and will contact the vendor to report the problem and to make any necessary arrangements for exchange, return authorization, credit, etc.

Suppliers are subject to re-evaluation, as deemed appropriate, through a review of complaints the laboratory had against the vendor in the previous 12 months.

The laboratory has access to a listing of all approved suppliers of critical consumables, supplies and services. This information is provided through the Coupa purchasing system.

11.6.1 New Vendor Procedure

Laboratory employees who wish to request the addition of a new vendor must complete a Vendor Add Request Form.

New vendors are evaluated based upon criteria appropriate to the products or services provided as well as their ability to provide those products and services at a competitive cost. Vendors are also evaluated to determine if there are ethical reasons or potential conflicts of interest with laboratory employees that would make it prohibitive to do business with them as well as their financial stability. The QA Department and/or Technical Services Director are consulted with vendor and product selection that have an impact on quality.

Vendors of critical supplies and services must be evaluated to ensure that their required ISO certification(s) are current and they meet any other laboratory specific criteria. Laboratory QA will add vendors who meet criteria to the Approved Vendors List for their site.

Table 11-1.

Storage of Reagents and Chemicals

Chemical	Storage Requirements
Concentrated Acids and Bases	Stored in the original containers at room temperature. All organic acids must be stored separately from inorganic acids. Acids should not be stored with bases.
Bulk Dry Chemicals	Stored in the original containers at room temperature. All organic acids must be stored separately from inorganic acids. Acids should not be stored with bases.
Working Solutions containing Organic Compounds	Stored as per method recommendation/ requirement. They are generally stored refrigerated at 4°C± 2°C (greater than freezing and < 6°C).
Working Solutions containing only Inorganics	Stored at room temperature; refrigeration is optional.
Flammable Solvents	Stored in solvent cabinets at room temperature.
Non-Flammable Solvents	Stored separately from the flammable solvents in cabinets at room temperature.

Note: Exceptions to the above detailed storage requirements may be made.

SECTION 12

COMPLAINTS

12.1 OVERVIEW

The laboratory considers an effective client complaint handling process to be of significant business and strategic value. Listening to and documenting client concerns captures client knowledge that enables our operations to continually improve processes and client satisfaction. An effective client complaint handling process also provides assurance to the data user that the laboratory will stand behind its data, service obligations and products.

A client complaint is any expression of dissatisfaction with any aspect of our business services, (e.g., communications, responsiveness, data, reports, invoicing and other functions) expressed by any party, whether received verbally or in written form. Client inquiries, complaints or noted discrepancies are documented, communicated to management, and addressed promptly and thoroughly.

The laboratory has procedures for addressing with both external and internal complaints with the goal of providing satisfactory resolution to complaints in a timely and professional manner.

The nature of the complaint is identified, documented and investigated, and an appropriate action is determined and taken. In cases where a client complaint indicates that an established policy or procedure was not followed, the QA Department must evaluate whether a special audit must be conducted to assist in resolving the issue. A written confirmation or letter to the client, outlining the issue and response taken is recommended as part of the overall action taken.

The process of complaint resolution and documentation utilizes the procedures outlined in Section 14 (Corrective Actions) and is documented following SOP UP-QA-029, Corrective Action Reports/ Non- Conformance Memos and Preventive Action Measures. It is the laboratory's goal to provide a satisfactory resolution to complaints in a timely and professional manner. A copy of this procedure will be made available to any interested party on request.

12.2 EXTERNAL COMPLAINTS

An employee that receives a complaint initiates the complaint resolution process by first documenting the complaint according to SOP UP-QA-029, Corrective Action Reports/ Non-Conformance Memos and Preventive Action Measures

Complaints fall into two categories: correctable and non-correctable. An example of a correctable complaint would be one where a report re-issue would resolve the complaint. An example of a non-correctable complaint would be one where a client complains that their data was repeatedly late. Non-correctable complaints should be reviewed for preventive action measures to reduce the likelyhood of future occurrence and mitigation of client impact.

The general steps in the complaint handling process are:

- Receiving and Documenting Complaints
- Acknowledging receipt of complaint, whenever possible
- Complaint Investigation and Service Recovery
- Process Improvement

The laboratory shall inform the initiator of the complaint of the results of the investigation and the corrective action taken, if any.

12.3 INTERNAL COMPLAINTS

Internal complaints include, but are not limited to: errors and non-conformances, training issues, internal audit findings, and deviations from methods. Corrective actions may be initiated by any staff member who observes a nonconformance and shall follow the procedures outlined in Section 14. In addition, Executive Management, Sales and Marketing and IT may initiate a complaint by contacting the laboratory or through the corrective action system described in Section 14.

12.4 MANAGEMENT REVIEW

The number and nature of client complaints is reported by the QA Manager to the Laboratory Director and Quality Director in the QA Monthly report. Monitoring and addressing the overall level and nature of client complaints and the effectiveness of the solutions is part of the Annual Management Systems Review (Section 18).

SECTION 13

CONTROL OF NON-CONFORMING WORK

13.1 OVERVIEW

When data discrepancies are discovered or deviations and departures from laboratory SOPs, policies and/or client requests have occurred, corrective action is taken immediately. First, the laboratory evaluates the significance of the nonconforming work. Then, a corrective action plan is initiated based on the outcome of the evaluation. If it is determined that the nonconforming work is an isolated incident, the plan could be as simple as adding a qualifier to the final results and/or making a notation in the case narrative. If it is determined that the nonconforming work is a systematic or improper practices issue, the corrective action plan could include a more in depth investigation and a possible suspension of an analytical method. In all cases, the actions taken are documented using the laboratory's corrective action system (refer to Section 14).

Due to the frequently unique nature of environmental samples, sometimes departures from documented policies and procedures are needed. When an analyst encounters such a situation, the problem is presented to the supervisor for resolution. The supervisor may elect to discuss it with the Project Manager, Technical Director, QA Manager or have a representative contact the client to decide on a logical course of action. Once an approach is agreed upon, the analyst documents it using the laboratories corrective action system described in Section 14. This information can then be supplied to the client in the case narrative with the report.

Project Management may encounter situations where a client may request that a special procedure be applied to a sample that is not standard lab practice. Based on a technical evaluation, the lab may accept or opt to reject the request based on technical or ethical merit. An example might be the need to report a compound that the lab does not normally report. The lab would not have validated the method for this compound following the procedures in Section 19. The client may request that the compound be reported based only on the calibration. Such a request would need to be approved by the Department Manager/Supervisor and QA Manager/Technical Director. Documentation detailing the method deviation must be included in the project folder. Deviations **must** also be noted on the final report with a statement that the compound is not reported in compliance with TNI (or the analytical method) requirements and the reason. (The laboratory will use a Non-Conformance Memo (NCM) in LIMS, which will be designated to print on the final report in the case narrative). Data being reported to a non-TNI state would need to note the change made to how the method is normally run.

13.2 RESPONSIBILITIES AND AUTHORITIES

Under certain circumstances the Laboratory Director, a Technical Manager, or a member of the QA team may authorize departures from documented procedures or policies. The departures may be a result of procedural changes due to the nature of the sample; a one-time procedure for a client; QC failures with insufficient sample to reanalyze, etc. In most cases, the client will be informed of the departure prior to the reporting of the data. Any departures must be well documented using the laboratory's corrective action procedures described in Section 14. This information may also be documented in logbooks and/or data review checklists and on a Non-Conformance Memo (NCM) in LIMS as appropriate. Any impacted data must be referenced in a case narrative and/or flagged with an appropriate data qualifier.

Any misrepresentation or possible misrepresentation of analytical data discovered by any laboratory staff member must be reported to facility Senior Management within 24-hours. The Senior Management staff is comprised of the Laboratory Director, the QA Manager, and the Technical Managers. The reporting of issues involving alleged violations of the company's Data Integrity or Manual Integration procedures must be conveyed to an ECO (e.g., the VP-QA/EHS) and the laboratory's Quality Director within 24 hours of discovery.

Whether an inaccurate result was reported due to calculation or quantitation errors, data entry errors, improper practices, or failure to follow SOPs, the data must be evaluated to determine the possible effect.

The Laboratory Director, QA Manager, ECOs, VP of Operations, VP of Operations and the Quality Directors have the authority and responsibility to halt work, withhold final reports, or suspend an analysis for due cause as well as authorize the resumption of work.

13.3 EVALUATION OF SIGNIFICANCE AND ACTIONS TAKEN

For each nonconforming issue reported, an evaluation of its significance and the level of management involvement needed is made. This includes reviewing its impact on the final data, whether or not it is an isolated or systematic issue, and how it relates to any special client requirements.

The NDSC Document entitled Nonconforming Work (QA-SOP38229) is the procedure to be followed when it is discovered that erroneous or biased data may have been reported to clients or regulatory agencies.

The NDSC Document entitled Ethics and Data Integrity Policy (QA-SOP38228) is the procedure to be followed for investigation and correction of situations involved alleged incidents of misconduct or violation of the company's ethics policy.

Laboratory level decisions are documented and approved using the laboratory's standard nonconformance/corrective action reporting in lieu of the data recall determination form contained in NDSC Document No. QA-SOP38229, Nonconforming Work.

13.4 PREVENTION OF NONCONFORMING WORK

If it is determined that the nonconforming work could recur, further corrective actions must be made following the laboratory's corrective action system (Section 14). Periodically as defined by the laboratory's preventive action schedule. The QA Department evaluates non-conformances to determine if any nonconforming work has been repeated multiple times. If so, the laboratory's corrective action process may be followed.

13.5 METHOD SUSPENSION/RESTRICTION (STOP WORK PROCEDURES)

In some cases it may be necessary to suspend/restrict the use of a method or target analyte which constitutes significant risk and/or liability to the laboratory. Suspension/restriction procedures can be initiated by any of the persons noted in Section 13.2, Paragraph 5 above.

Prior to suspension/restriction, confidentiality will be respected, and the problem with the required corrective and preventive action will be stated in writing and presented to the Laboratory Director.

The Laboratory Director shall arrange for the appropriate personnel to meet with the QA Manager as needed. This meeting shall be held to confirm that there is a problem, that suspension/restriction of the method is required and will be concluded with a discussion of the steps necessary to bring the method/target or test fully back on line. In some cases that may not be necessary if all appropriate personnel have already agreed there is a problem and there is agreement on the steps needed to bring the method, target or test fully back on line.

The QA Manager will also initiate a corrective action report as described in Section 14 if one has not already been started. A copy of any meeting notes and agreed upon steps should be e-mailed by the laboratory to their Business Unit President; VP-QA & EH&S. This e-mail acts as notification of the incident.

After suspension/restriction, the lab will hold all reports to clients pending review. No faxing, mailing or distributing through electronic means may occur. The report must not be posted for viewing on the internet. It is the responsibility of the Laboratory Director to hold all reporting and to notify all relevant laboratory personnel regarding the suspension/restriction (i.e., Project Management, Log-in, etc…). Clients will NOT generally be notified at this time. Analysis may proceed in some instances depending on the non-conformance issue.

Within 72 hours, the QA Manager will determine if compliance is now met and reports can be released, OR determine the plan of action to bring work into compliance, and release work. A team, with all principals involved (e.g., Laboratory Director, QA Manager, Technical Manager) can devise a start-up plan to cover all steps from client notification through compliance and release of reports. Project Management and the Director of Client Services and Sales and Marketing **must** be notified if clients must be notified or if the suspension/restriction affects the laboratory's ability to accept work. The QA Manager must approve start-up or elimination of any restrictions after all corrective action is complete.

SECTION 14

CORRECTIVE ACTION

14.1 OVERVIEW

A major component of the laboratory's QA Program is the problem investigation and feedback mechanism designed to keep the laboratory staff informed on quality related issues and to provide insight to problem resolution. When nonconforming work or departures from policies and procedures in the quality system or technical operations are identified, the corrective action procedure provides a systematic approach to assess the issues, restore the laboratory's system integrity, and prevent reoccurrence. The laboratory employs two systems to manage non-conformances. Issues suspected of being systematic in nature and for which root cause analysis and a formal Corrective Action Report (CAR) are documented in the Incident Corrective Action Tracking (ICAT) database. Routine batch non-conformances, events that are understood to be isolated in nature, are documented in the TALS non-conformance memo (NCM) system.

14.2 GENERAL

Problems within the quality system or within analytical operations may be discovered in a variety of ways, such as QC sample failures, internal or external audits, proficiency testing (PT) performance, client complaints, staff observation, etc.

The purpose of a corrective action system is to:

- Identify non-conformance events and assign responsibility(s) for investigating.
- Resolve non-conformance events and assign responsibility for any required corrective action.
- Identify systematic problems before they become serious.
- Identify and track client complaints and provide resolution

14.2.1 Non-Conformance Memo (NCM)

NCMs are used to document the following types of corrective actions:

- Deviations from an established procedure or SOP
- QC outside of limits
- Missed sample Holding Times
- Isolated Reporting / Calculation Errors
- Client complaints
- Discrepancies in materials / good received vs. manufacturer packing slips. (Forms of documentation other than NCMs in TALS are also acceptable).

14.2.2 Corrective Actions Documented in the ICAT Database

- Internal and external audit findings
- Failed or unacceptable PT results
- Identified poor process or method performance trends
- Systematic reporting / calculation errors
- Data recall investigations
- Questionable trends that are found in the review of NCMs.
- Client complaints
- Excessive revised reports

The laboratory's corrective action database is used to document background information, track the results of corrective action investigations and root cause analysis, and to provide reports of corrective action plans.

14.3 CLOSED LOOP CORRECTIVE ACTION PROCESS

Any employee in the company can initiate a corrective action. There are four main components to a closed-loop corrective action process once an issue has been identified: Cause Analysis, Selection and Implementation of Corrective Actions (both short and long term), Monitoring of the Corrective Actions, and Follow-up.

14.3.1 Cause Analysis

- Upon discovery of a non-conformance event, the event must be defined and documented. An entry into the laboratory's corrective action spreadsheet must be initiated, someone is assigned to investigate the issue and the event is investigated for cause. Table 14-1, and Appendix 4 tables provide some general guidelines on determining responsibility for assessment.

- The cause analysis step is the key to the process as a long term corrective action cannot be determined until the cause is determined.
- If the cause is not readily obvious, the Technical Manager, Laboratory Director, Project Manager or QA Manager (or QA designee) is consulted.

14.3.2 Selection and Implementation of Corrective Actions

- Where corrective action is needed, the laboratory shall identify potential corrective actions. The action(s) most likely to eliminate the problem and prevent recurrence are selected and implemented. Responsibility for implementation is assigned.
- Corrective actions shall be to a degree appropriate to the magnitude of the problem identified through the cause analysis.
- Whatever corrective action is determined to be appropriate, the laboratory shall document and implement the changes. The laboratory's corrective action spreadsheet is used for this documentation.

14.3.3 Root Cause Analysis

Root Cause Analysis is a class of problem solving (investigative) methods aimed at identifying the basic or causal factor(s) that underlie variation in performance or the occurrence of a significant failure. The root cause may be buried under seemingly innocuous events, many steps preceding the perceived failure. At first glance, the immediate response is typically directed at a symptom and not the cause. Typically, root cause analysis would be best with three or more incidents to triangulate a weakness. NDSC Document No. NDSC-QA-SOP43847, Root Cause Analysis, provides guidance on this procedure.

Systematically analyze and document the Root Causes of the more significant problems that are reported. Identify, track, and implement the corrective actions required to reduce the likelihood of recurrence of significant incidents. Trend the Root Cause data from these incidents to identify Root Cause that, when corrected, can lead to dramatic improvements in performance by eliminating entire classes of problems.

Identify the one event associated with problem and ask why this event occurred. Brainstorm the root causes of failures; for example, by asking why events occurred or conditions existed; and then why the cause occurred consecutive times until you get to the root cause. For each of these sub events or causes, ask why it occurred. Repeat the process for the other events associated with the incident.

Root cause analysis does not mean the investigation is over. Look at technique, or other systems outside the normal indicators. Often creative thinking will find root causes that ordinarily would be missed, and continue to plague the laboratory or operation.

14.3.4 Monitoring of the Corrective Actions

- The Technical Managers and the QA Manager are responsible to ensure that the corrective action taken was effective.
- Ineffective actions are documented and re-evaluated until acceptable resolution is achieved. Technical Managers are accountable to the Laboratory Director to ensure final acceptable resolution is achieved and documented appropriately.
- The QA Manager reviews monthly NCMs and the laboratory's corrective action spreadsheet for trends. Highlights are included in the QA monthly report (refer to Section 18). If a significant trend develops that adversely affects quality, an audit of the area is performed and corrective action implemented.

- Any out-of-control situations that are not addressed acceptably at the laboratory level may be reported to the NDSC Quality Director by the QA Manager, indicating the nature of the out-of-control situation and problems encountered in solving the situation.

14.3.5 Follow-up Audits

- Follow-up audits may be initiated by the QA Manager and shall be performed as soon as possible when the identification of a nonconformance casts doubt on the laboratory's compliance with its own policies and procedures, or on its compliance with state or federal requirements. (Section 17 includes additional information regarding internal audit procedures.)
- These audits often follow the implementation of the corrective actions to verify effectiveness. An additional audit would only be necessary when a critical issue or risk to business is discovered. (Also refer to Section 17.1.4, Special Audits.)

14.4 TECHNICAL CORRECTIVE ACTIONS

In addition to providing acceptance criteria and specific protocols for technical corrective actions in the method specific SOPs, and in the Appendix 4 tables, the laboratory has general procedures to be followed to determine when departures from the documented policies and procedures and quality control have occurred (refer to Section 13 for information regarding the control of non-conforming work). The documentation of these procedures is through the use of an NCM.

Table 14-1 includes examples of general technical corrective actions. For specific criteria and corrective actions refer to the analytical methods or specific method SOPs. Appendix 4 of this QAM also summarizes QC requirements and corrective actions for the methods run in the lab.

Table 14-1 provides some general guidelines for identifying the individual(s) responsible for assessing each QC type and initiating corrective action. The table also provides general guidance on how a data set should be treated if associated QC measurements are unacceptable. Specific procedures are included in Method SOPs, Work Instructions, and QA Manual Appendix 4, Sections 19 and 20. All corrective actions are reviewed at a minimum monthly by the QA Manager and highlights are included in the QA monthly report.

To the extent possible, samples shall be reported only if all quality control measures are acceptable. If the deficiency does not impair the usability of the results, data will be reported with an appropriate data qualifier and/or the deficiency will be noted in the case narrative. Where sample results may be impaired, the Project Manager is notified by an NCM as appropriate corrective action (e.g., reanalysis) is taken and documented.

14.5 BASIC CORRECTIONS

When mistakes occur in records, each mistake shall be crossed-out, [not obliterated (e.g. no white-out)], and the correct value entered alongside. All such corrections shall be initialed (or signed) and dated by the person making the correction. In the case of records stored electronically, the original uncorrected file must be maintained intact and a second corrected file is created. This same process applies to adding additional information to a record. All additions made later than the initial must also be initialed (or signed) and dated. When corrections are due to reasons other than obvious transcription errors, the reason for the corrections (or additions) shall also be documented.

Table 14-1.

Example – General Corrective Action Procedures

QC Activity ***(Individual Responsible for Initiation/Assessment)***	**Acceptance Criteria**	**Recommended Corrective Action**
Proficiency Testing (PT) Samples *(QA Manager, QA Specialist, Technical Manager)*	- Criteria supplied by PT Supplier.	- Any failures or warnings must be entered into the internal corrective action system, investigated for root cause and all necessary corrections must be made to prevent a repeat of the PT Failure. Failures may result in the need to repeat a PT sample to show the problem has been corrected.
Internal / External Audits *(QA Manager, QA Specialist, Technical Manager, Laboratory Director)*	- Defined in Quality System documentation such as SOPs, QAM, etc.	- Non-conformances must be entered into the CAR system, investigated for root cause and any necessary corrections must be made to prevent a repeat of the non-conformance event.
Reporting / Calculation Errors (Depends on issue – possible individuals include: Analysts, Data Reviewers, Project Managers, Technical Manager, QA Manager, NDSC QA, Executive Management)	NDSC Document No. QA-SOP38229, Nonconforming Work.	- Corrective action is determined by type of error. Follow the procedures in NDSC Document No. QA-SOP38229.
Client Complaints *(Project Managers, Lab Director, Sales and Marketing, QA Manager, Technical Manager)*	-	- Corrective action is determined by the type of complaint. For example, a complaint regarding an incorrect address on a report will result in the report being corrected and then follow-up must be performed on the reasons the address was incorrect (e.g., database needs to be updated).
QA Monthly Report (QA Manager, Lab Director)	- QAM, SOPs.	- Corrective action is determined by the type of issue. For example, NCMs are reviewed periodically and possible trends are investigated.
Health and Safety Violation (Safety Officer, Lab Director, Technical Manager)	- Environmental Health and Safety (EHS) Manual.	- Non-conformance is investigated and corrected through CAR system.

SECTION 15

PREVENTIVE ACTION / IMPROVEMENT

15.1 OVERVIEW

The laboratory's preventive action programs improve, or eliminate potential causes of nonconforming product and/or nonconformance to the quality system. This preventive action process is a proactive and continuous process of improvement activities that can be initiated through feedback from clients, employees, business providers, and affiliates. The QA Department has the overall responsibility to ensure that the preventive action process is in place, and that relevant information on actions is submitted for management review.

Dedicating resources to an effective preventive action system emphasizes the laboratory's commitment to its QA Program. It is beneficial to identify and address negative trends before they develop into complaints, problems and corrective actions. Additionally, customer service and client satisfaction can be improved through continuous improvements to laboratory systems.

Opportunities for improvement may be discovered through any of the following:

- review of the monthly QA Metrics Report,
- trending NCMs,
- review of control charts and QC results,
- trending proficiency testing (PT) results,
- performance of management system reviews,
- trending client complaints,
- review of processing operations, or
- staff observations.

The monthly Management Systems Metrics Report shows performance indicators in all areas of the laboratory and quality system. These areas include revised reports, corrective actions, audit findings, internal auditing and data authenticity audits, client complaints, PT samples, holding time violations, SOPs, ethics training, etc. The metrics report is reviewed monthly by the laboratory management, NDSC QA Team, Local and Executive Management. These metrics are used in evaluating the management and quality system performance on an ongoing basis and provide a tool for identifying areas for improvement.

Items identified as continuous improvement opportunities to the management system may be issued as goals from the annual management systems review, recommendations from internal audits, white papers, Lessons Learned, Technical Services audit report, Technical Best Practices, or as Executive or management initiatives.

The laboratory's corrective action process is integral to implementation of preventive actions. A critical piece of the corrective action process is the implementation of actions to prevent further occurrence of a non-compliance event. Historical review of corrective action provides a valuable mechanism for identifying preventive action opportunities.

15.1.1 The following elements are part of a preventive action system:

- Identification of an opportunity for preventive action.
- Process for the preventive action.
- Define the measurements of the effectiveness of the process once undertaken.
- Execution of the preventive action.
- Evaluation of the plan using the defined measurements.

- Verification of the effectiveness of the preventive action.
- Close-Out by documenting any permanent changes to the Quality System as a result of the Preventive Action. Documentation of Preventive Action is incorporated into the monthly QA reports, corrective action process and management review.

Note: There may be varying levels of formality and documentation during the preventive action process due to the simplicity/complexity of the action taken.

15.1.2 Any Preventive Actions undertaken or attempted shall be taken into account during the Annual Management Systems Review (Section 18.2). A highly detailed report is not required; however, a simple summary of successes and failures within the preventive action program is sufficient to provide management with a measurement for evaluation.

15.2 MANAGEMENT OF CHANGE

The Management of Change process is designed to manage significant events and changes that occur within the laboratory. Through these various tracking indicators, the potential risks inherent with a new event or change are identified and evaluated. The risks are minimized or eliminated through pre-planning and the development of preventive measures. The types of indicators monitored under this collective system include: Facility Changes, Major Accreditation Changes, Addition or Deletion to Division's Capabilities or Instrumentation, Key Personnel Changes, Laboratory Information Management System (LIMs) changes.

SECTION 16

CONTROL OF RECORDS

The laboratory maintains a records management system appropriate to its needs and that complies with applicable standards or regulations as required. The system produces unequivocal, accurate records that document all laboratory activities. The laboratory retains all original observations, calculations and derived data, calibration records and a copy of the analytical report for a minimum of five years after it has been issued. Exceptions for programs with longer retention requirements are discussed in Section 16.2. Refer to laboratory *SOPs UP-DM-002,* Data Management: Record Retention & Purging and *UP-IS-006,* Processes Entry, Storage, Backup/Retrieval, Mgmt Bench Data for further details.

16.1 OVERVIEW

The laboratory has established procedures for identification, collection, indexing, access, filing, storage, maintenance and disposal of quality and technical records. A record index is listed in Table 16-1. More detailed information on retention of specific records is provided in CW-L-P-001, Records Retention Policy and CW-L-WI-001, Eurofins Records Retention/Storage Schedule. Quality records are maintained by the QA department on the local area network (LAN) in the \\tacorp\Corp\QA\QA_Facilities\Chicago-QA directory and the data files are backed up as part of the regular laboratory backup. Records are of two types; either electronic or hard copy paper formats depending on whether the record is computer or hand generated (some records may be in both formats). Technical records are maintained in accordance with the SOP UP-DM-002 *Data Management: Record Retention and Purging*

Table 16-1. Record Index[1]

Record Type[1]		Retention Time:
Technical Records	-Raw Data -Logbooks[2] -Standards -Certificates -Analytical Records -PTs/MDLs/IDLs/DOCs -Lab Reports	5 years from analytical report issue*
Official Documents	- Quality Assurance Manual (QAM) - Work Instructions - Policies - SOPs - Policy Memorandums - Manuals - Published Methods	Indefinitely
QA Records	- Certifications - Method and Software Validation / Verification Data	Indefinitely
QA Records	Internal & External Audits/Responses Corrective/Preventive Actions/NCMs Management Reviews Review Checklists Statistical Evaluations Data Investigation	5 Years from archival* Data Investigation: 5 years or the life of the affected raw data storage whichever is greater (beyond 5 years if ongoing project or pending investigation)
Project Records	Sample Receipt & COC Documentation Contracts & Amendments Correspondence QAPP SAP Telephone Logs E-mail correspondence Lab Reports Electronic Data (EDD)	5 Years from analytical report issue*
Administrative Records	Financial and Business Operations	Refer to NDSC SOP. NDSC-US-LEG-FRM58366
	EH&S Manual, Permits	Indefinitely
	Disposal Records, Permits	Indefinitely
	Employee Handbook	Indefinitely
	Personnel files, Employee Signature & Initials, Administrative Training Records (e.g., Ethics)	Refer to HR Manual
	Administrative Policies	Indefinitely
	Technical Training Records	7 years
	Legal Records	Indefinitely
	HR Records	Refer to NDSC SOP. NDSC-US-LEG-FRM58366
	IT Records	Refer to NDSC SOP. NDSC-US-LEG-FRM58366
	NDSC Governance Records	Refer to NDSC SOP. NDSC-US-LEG-FRM58366
	Sales & Marketing	5 years
	Real Estate	Indefinitely

[1] Record Types encompass hardcopy and electronic records.

[2] Examples of Logbook types: Maintenance, Instrument Run, Preparation (standard and samples), Standard and Reagent Receipt, Archiving, Balance Calibration, Temperature (hardcopy or electronic records).

* Exceptions listed in Table 16-2.

16.1.1 All records are legible and stored and retained in such a way that they are secure and readily retrievable at the laboratory facility or the offsite location that provides a suitable environment to prevent damage or deterioration and to prevent loss. All records shall be protected against fire, theft, loss, environmental deterioration, and vermin. In the case of electronic records, electronic or magnetic sources, storage media are protected from deterioration caused by magnetic fields and/or electronic deterioration.

Access to the data is limited to laboratory and company employees and shall be documented with an access log. Records archived off-site are stored in a secure location where a record is maintained of any entry into the storage facility. Whether on-site or off-site storage is used, logs are maintained in each storage box to note removal and return of records. Retention of records are maintained on-site at the laboratory for at least 1 year after their generation and moved off-site for the remainder of the required storage time. Records are maintained for a minimum of five years unless otherwise specified by a client or regulatory requirement.

For raw data and project records, record retention shall be calculated from the date the project report is issued. For other records, such as NDSC and/or KGD Documents, QA, or Administrative Records, the retention time is calculated from the date the record is formally retired. Records related to the programs listed in Table 16-2 have lengthier retention requirements and are subject to the requirements in Section 16.2.

16.2 Programs with Longer Retention Requirements

Some regulatory programs have longer record retention requirements than the standard record retention time. These are detailed in Table 16-2 with their retention requirements. In these cases, the longer retention requirement is enacted. If special instructions exist such that client data cannot be destroyed prior to notification of the client, the container or box containing that data is marked as to who to contact for authorization prior to destroying the data.

Table 16-2. Example: Special Record Retention Requirements

Program	[1]Retention Requirement
Drinking Water – All States	10 years (lab reports and raw data) 10 years - Radiochemistry (project records)
Drinking Water Lead and Copper Rule	12 years (project records)
Commonwealth of MA – All environmental data 310 CMR 42.14	10 years
FIFRA – 40 CFR Part 160	Retain for life of research or marketing permit for pesticides regulated by EPA
Housing and Urban Development (HUD) Environmental Lead Testing	10 years
Alaska	10 years
Louisiana – All	10 years
Michigan Department of Environmental Quality – all environmental data	10 years
Navy Facilities Engineering Service Center (NFESC)	10 years
Ohio VAP	10 years and State contacted prior to disposal
OSHA	30 years

[1]Note: Extended retention requirements must be noted with the archive documents or addressed in facility-specific records retention procedures.

16.2.1 The laboratory has procedures to protect and back-up records stored electronically and to prevent unauthorized access to or amendment of these records. All analytical data is

maintained as hard copy or in a secure readable electronic format. For analytical reports that are maintained as copies in PDF format, refer to Section 19.15.1 for more information. Refer to the laboratory SOP *UP-DM-002 - Data Management: Record Retention and Purging* for the discussion on electronic archiving and the maintenance of electronic records.

16.2.2 The record keeping system allows for historical reconstruction of all laboratory activities that produced the analytical data, as well as rapid recovery of historical data (Records stored off site should be accessible within 2 days of a request for such records). The history of the sample from when the laboratory took possession of the samples must be readily understood through the documentation. This shall include inter-laboratory transfers of samples and/or extracts.

- The records include the identity of personnel involved in sampling, sample receipt, preparation, or testing. All analytical work contains the initials (at least) of the personnel involved. The laboratory's copy of the COC is stored with the invoice and the work order sheet generated by LIMs and can be accessed via the Project Management Desktop. The chain of custody (COC) would indicate the name of the sampler. If any sampling notes are provided with a work order, they are kept with this package. The COC is filed separately by Job number in the data management department. A copy of the COC is included as part of every data report.
- All information relating to the laboratory facilities equipment, analytical test methods, and related laboratory activities, such as sample receipt, sample preparation, or data verification are documented.
- The record keeping system facilitates the retrieval of all working files and archived records for inspection and verification purposes (e.g., set format for naming electronic files, set format for what is included with a given analytical data set refer to laboratory SOP UP-IS-006, *Processes Entry, Storage, Backup/Retrieval, Mgmt Bench Data* for further details. Instrument data is stored sequentially by instrument. A given day's analyses are maintained in the order of the analysis. Run logs are maintained for each instrument or method; a copy of each day's run log or instrument sequence is stored with the data to aid in re-constructing an analytical sequence. Where an analysis is performed without an instrument, bound logbooks or bench sheets are used to record and file data. Standard and reagent information is recorded in logbooks or entered into the LIMS for each method as required.
- Changes to hardcopy records shall follow the procedures outlined in Section 14 and 19. Changes to electronic records in TALs or instrument data are recorded in audit trails.
- The reason for a signature or initials on a document is clearly indicated in the records such as "sampled by," "prepared by," "reviewed by", or "Analyzed by".
- All generated data except those that are generated by automated data collection systems, are recorded directly, promptly and legibly in permanent dark ink.
- Hard copy data may be scanned into PDF format for record storage as long as the scanning process can be verified in order to ensure that no data is lost and the data files and storage media must be tested to verify the laboratory's ability to retrieve the information prior to the destruction of the hard copy that was scanned. The procedure for this verification can be found in the laboratory SOP *UP-DM-002 – Data Management: Record Retention and Purging.*
- Also refer to Section 19.15.1 'Computer and Electronic Data Related Requirements'.

16.3 TECHNICAL AND ANALYTICAL RECORDS

16.3.1 The laboratory retains records of original observations, derived data and sufficient information to establish an audit trail, calibration records, staff records and a copy of each analytical report issued, for a minimum of five years unless otherwise specified by a client or

regulatory requirement. The records for each analysis shall contain sufficient information to enable the analysis to be repeated under conditions as close as possible to the original. The records shall include the identity of laboratory personnel responsible for the sampling, preparation and performance of each analysis and reviewing results.

16.3.2 Observations, data and calculations are recorded real-time and are identifiable to the specific task.

16.3.3 Changes to hardcopy records shall follow the procedures outlined in Section 13 and 19. Changes to electronic records in LIMs or instrument data are recorded in audit trails.

The essential information to be associated with analysis, such as strip charts, tabular printouts, computer data files, analytical notebooks, and run logs, include:

- laboratory sample ID code**;**
- Date of analysis and Time of Analysis is also required if the holding time is seventy-two (72) hours or less, or when time critical steps are included in the analysis (e.g., drying times, incubations, etc.); instrumental analyses have the date and time of analysis recorded as part of their general operations. Where a time critical step exists in an analysis, location for such a time is included as part of the documentation in a specific logbook or worksheet and in the TALs system**.**
- Instrumentation identification and instrument operating conditions/parameters. Operating conditions/parameters are typically recorded in instrument maintenance logs where available.
- analysis type**;**
- all manual calculations and manual integrations**;**
- analyst's or operator's initials/signature**;**
- sample preparation including cleanup, separation protocols, incubation periods or subculture, ID codes, volumes, weights, instrument printouts, meter readings, calculations, reagents**;**
- test results**;**
- standard and reagent origin, receipt, preparation, and use**;**
- calibration criteria, frequency and acceptance criteria**;**
- data and statistical calculations, review, confirmation, interpretation, assessment and reporting conventions**;**
- quality control protocols and assessment**;**
- electronic data security, software documentation and verification, software and hardware audits, backups, and records of any changes to automated data entries; and
- Method performance criteria including expected quality control requirements. These are indicated both in LIMs and on specific analytical report formats**.**

16.3.4 All logbooks used during receipt, preparation, storage, analysis, and reporting of samples or monitoring of support equipment shall undergo a periodic, documented supervisory or peer review.

16.4 LABORATORY SUPPORT ACTIVITIES

In addition to documenting all the above-mentioned activities, the following are retained QA records and project records (previous discussions in this section relate where and how these data are stored):

- all original raw data, whether hard copy or electronic, for calibrations, samples and quality

control measures, including analysts' work sheets and data output records (chromatograms, strip charts, and other instrument response readout records);

- a written description or reference to the specific test method used which includes a description of the specific computational steps used to translate parametric observations into a reportable analytical value;
- copies of final reports;
- archived SOPs;
- correspondence relating to laboratory activities for a specific project;
- all corrective action reports, audits and audit responses;
- proficiency test results and raw data; and
- results of data review, verification, and crosschecking procedures

16.4.1 Sample Handling Records

Records of all procedures to which a sample is subjected while in the possession of the laboratory are maintained. These include but are not limited to records pertaining to:

- sample preservation including appropriateness of sample container and compliance with holding time requirement;
- sample identification, receipt, acceptance or rejection and login;
- sample storage and tracking including shipping receipts, sample transmittal / COC forms; and
- procedures for the receipt and retention of samples, including all provisions necessary to protect the integrity of samples.

16.5 ADMINISTRATIVE RECORDS

The laboratory also maintains the administrative records in either electronic or hard copy form. See Table 16-1.

16.6 RECORDS MANAGEMENT, STORAGE AND DISPOSAL

16.6.1 All records (including those pertaining to test equipment), certificates and reports are safely stored, held secure and in confidence to the client. Certification related records are available to the accrediting body upon request.

16.6.2 All information necessary for the historical reconstruction of data is maintained by the laboratory. Records that are stored only on electronic media must be supported by the hardware and software necessary for their retrieval.

16.6.3 Records that are stored or generated by computers or personal computers have hard copy, write-protected backup copies, or an electronic audit trail controlling access.

16.6.4 The laboratory has a record management system (a.k.a., document control) for control of laboratory notebooks, instrument logbooks, and records for data reduction, validation, storage and reporting. Laboratory bound notebooks are issued on a per analysis basis, and pages are numbered sequentially. All data are recorded sequentially within a series of sequential notebooks. Bench sheets, when used, are filed with any subsequent raw data by Department and sequentially by the LIMs Batch number. Standards are maintained in the LIMs reagent module. Records are considered archived when noted as such in the records management system (a.k.a., document control).

16.6.5 Transfer of Ownership

In the event that the laboratory transfers ownership or goes out of business, the laboratory shall

ensure that the records are maintained or transferred according to client's instructions. Upon ownership transfer, record retention requirements shall be addressed in the ownership transfer agreement and the responsibility for maintaining archives is clearly established. In addition, in cases of bankruptcy, appropriate regulatory and state legal requirements concerning laboratory records must be followed. In the event of the closure of the laboratory, all records will revert to the control of the NDSC. Should the entire company cease to exist, as much notice as possible will be given to clients and the accrediting bodies who have worked with the laboratory during the previous 5 years of such action.

16.6.6 Records Disposal

16.6.6.1 Records are removed from the archive and destroyed after 5 years unless otherwise specified by a client or regulatory requirement. On a project specific or program basis, clients may need to be notified prior to record destruction. Records are destroyed in a manner that ensures their confidentiality such as shredding, mutilation or incineration (Refer to Tables 16-1 and 16-2).

16.6.6.2 Electronic copies of records must be destroyed by erasure or physically damaging off-line storage media so no records can be read.

16.6.6.3 If a third party records management company is hired to dispose of laboratory records, a "Certificate of Destruction" is required.

SECTION 17

AUDITS

17.1 INTERNAL AUDITS

Internal audits are performed to verify that laboratory operations comply with the requirements of the lab's quality system and with the external quality programs under which the laboratory operates. Audits are planned and organized by the QA staff. Personnel conducting the audits should be independent of the area being evaluated. Auditors will have sufficient authority, access to work areas, and organizational freedom necessary to observe all activities affecting quality and to report the assessments to laboratory management and when requested to Executive Management.

Audits are conducted and documented as described in the NDSC Document No. NDSC-QA-SOP5260 on performing Internal Auditing. The types and frequency of routine internal audits are described in Table 17-1. Special or ad hoc assessments may be conducted as needed under the direction of the QA staff.

Table 17-1. Types of Internal Audits and Frequency

Description	Performed by	Frequency
Quality System Audits	QA Department or QA approved designee, or Corporate QA	All areas of the laboratory annually
QA Technical Audits	Joint responsibility: a) QA Manager or Designee b) Technical Manager or Designee (Refer to NDSC-QA-SOP5260)	Technical Audit Frequency: 50% of methods annually

Description	Performed by	Frequency
SOP Method Compliance	Joint responsibility: a) QA Manager or Designee b) Technical Manager or Designee (Refer to NDSC-QA-SOP5260)	SOP Compliance Review Frequency: Every 2 years Every 1 year (Drinking Water Methods) 100% of SOPs annually (DoD/DOE Labs)
Special	QA Department or Designee	Surveillance or spot checks performed as needed, e.g., to confirm corrective actions from other audits.
Performance Testing	Analysts with QA oversight	Two successful per year for each TNI field of testing or as dictated by regulatory requirements

17.1.1 Annual Quality Systems Audit

An annual quality systems audit is required to ensure compliance to analytical methods and SOPs, Eurofins Data Integrity and Ethics Policies, (see Sec. 7.2) TNI quality systems, client and state requirements, and the effectiveness of the internal controls of the analytical process, including but not limited to data review, quality controls, preventive action and corrective action. The completeness of earlier corrective actions is assessed for effectiveness & sustainability. The audit is divided into sections for each operating or support area of the lab, and each section is comprehensive for a given area. The area audits may be performed on a rotating schedule throughout the year to ensure adequate coverage of all areas. This schedule may change as situations in the laboratory warrant.

17.1.2 QA Technical Audits

QA technical audits are based on client projects, associated sample delivery groups, and the methods performed. Reported results are compared to raw data to verify the authenticity of results. The validity of calibrations and QC results are compared to data qualifiers, footnotes, and case narratives. Documentation is assessed by examining run logs and records of manual integrations. Manual calculations are checked. Where possible, electronic audit miner program (e.g., Chrom AuditMiner) is used to identify unusual manipulations of the data deserving closer scrutiny. QA technical audits will include all methods within a two-year period.

17.1.3 SOP Method Compliance

Compliance of all SOPs with the source methods and compliance of the operational groups with the SOPs will be assessed by the Technical Manager or qualified designee at least every two years. (Annually for methods and administrative SOPs related to DoD/DOE programs and DW compliance methods – where applicable.) It is also recommended that the work of each newly hired analyst is assessed within 3 months of working independently, (e.g., completion of method IDOC). In addition, as analysts add methods to their capabilities, (new IDOC) reviews of the analyst work products will be performed within 3 months of completing the documented training.

17.1.4 Special Audits

Special audits are conducted on an as needed basis, generally as a follow up to specific issues such as client complaints, corrective actions, PT results, data audits, system audits, validation comments, regulatory audits or suspected ethical improprieties. Special audits are focused on a specific issue, and report format, distribution, and timeframes are designed to address the nature of the issue.

17.1.5 Performance Testing

The laboratory participates semi-annually in performance audits conducted through the analysis of PT samples provided by a third party. The laboratory generally participates in the following

types of PT studies: Drinking Water (WS), Non-potable Water (WP), Soil (SW), Sediment, and Hazardous Waste (HW).

It is Eurofins policy that PT samples be treated as typical samples in the production process. Furthermore, where PT samples present special or unique problems, in the regular production process they may need to be treated differently, as would any special or unique request submitted by any client. The QA Manager must be consulted and in agreement with any decisions made to treat a PT sample differently due to some special circumstance.

Written investigations for unacceptable PT results are required. In some cases it may be necessary for blind QC samples to be submitted to the laboratory to show a return to control.

17.1.6 Good Laboratory Practice Critical Phase Inspection

Any project that is subject to Good Laboratory Practice (GLP) regulations is audited by the QA Department, as required by the regulations, at intervals adequate to ensure the integrity of the study. Inspections of a GLP project include direct observation of analysts as they perform various phases of the study. Data documentation is reviewed as part of the inspection. The purpose of this type of audit is to ensure that there are no deviations from written methods, procedures, or study protocols.

Results of inspections are documented in a report format and distributed to applicable management personnel responsible for the area(s) under audit. Management is responsible to address all non-conformances found during an inspection. Inspection reports and responses are circulated to applicable laboratory management and an off-site study director, as applicable, to communicate the outcome of the inspection and the proposed plan(s) for corrective action, if warranted.

All records maintained as part of an inspection are kept on file

17.2 EXTERNAL AUDITS

External audits are performed when certifying agencies or clients conduct on-site inspections or submit performance testing samples for analysis. It is Eurofins policy to cooperate fully with regulatory authorities and clients. The laboratory makes every effort to provide the auditors with access to personnel, documentation, and assistance. Laboratory supervisors are responsible for providing corrective actions to the QA Manager who coordinates the response. Audit responses are due in the time allotted by the client or agency performing the audit.

The laboratory cooperates with clients and their representatives to monitor the laboratory's performance in relation to work performed for the client. The client may only view data and systems related directly to the client's work. All efforts are made to keep other client information confidential.

17.2.1 Confidential Business Information (CBI) Considerations

During on-site audits, on-site auditors may come into possession of information claimed as business confidential. A business confidentiality claim is defined as "a claim or allegation that business information is entitled to confidential treatment for reasons of business confidentiality or a request for a determination that such information is entitled to such treatment." When information is claimed as business confidential, the laboratory must place on (or attach to) the information at the time it is submitted to the auditor, a cover sheet, stamped or typed legend or other suitable form of notice, employing language such as "trade secret", "proprietary" or "company confidential". Confidential portions of documents otherwise non-confidential must be clearly identified. CBI may be purged of references to client identity by the responsible laboratory official at the time of removal from the laboratory. However, sample identifiers may not be obscured from the information. Additional information regarding CBI can be found in within the 2009 and 2016 TNI standards.

17.3 AUDIT FINDINGS

Audit findings are documented using the corrective action process and database (see Section 14). The laboratory's corrective action responses for both types of audits may include action plans that could not be completed within a predefined timeframe. In these instances, a completion date must be set and agreed to by operations management and the QA Manager.

Developing and implementing corrective actions to findings is the responsibility of the Technical Manager where the finding originated. Findings that are not corrected by specified due dates are reported monthly to management in the QA monthly report.

If any audit finding casts doubt on the effectiveness of the operations or on the correctness or validity of the laboratory's test results, the laboratory shall take timely corrective action, and shall notify clients in writing if the investigations show that the laboratory results have been affected. Once corrective action is implemented, a follow-up audit is scheduled to ensure that the problem has been corrected.

Clients must be notified promptly in writing, of any event such as the identification of defective measuring or test equipment that casts doubt on the validity of results given in any test report or amendment to a test report. The investigation must begin within 24-hours of discovery of the problem and all efforts are made to notify the client within two weeks after the completion of the investigation.

SECTION 18

MANAGEMENT REVIEWS

18.1 QUALITY ASSURANCE REPORT

The QA Department is responsible for preparing a comprehensive monthly metrics report to Management to keep them apprised of current quality issues. This report fosters communication, review, and refinement of the QA system to evaluate the suitability of policies and procedures to meet both regulatory and laboratory quality objectives.

The NDSC QA team compiles information from all of the Environment Testing laboratories monthly metrics reports for the Executive Management team. This report includes notable information and concerns regarding the laboratories QA program and a listing of new regulations that may potentially impact the laboratories.

18.2 ANNUAL MANAGEMENT REVIEW

The laboratory management team (Laboratory Director, QA Manager, Operations Manager and Technical Managers) conducts a review annually of its quality systems to ensure its continuing suitability and effectiveness in meeting client and regulatory requirements and to introduce any necessary changes or improvements. It will also provide a platform for defining goals & objectives and action items that feed into the laboratory's planning system. NDSC personnel may be included in this meeting at the discretion of the Laboratory Director. The LIMS review consists of examining any audits, complaints or concerns that have been raised throughout the year that are related to LIMS. The laboratory will summarize any critical findings that cannot be solved by the lab and report them to Corporate IT.

This management systems review (NDSC Document No. QA-QP38702, *Management Systems Review,* & Work Instruction No. NDSC-QA-FRM43453) uses information generated during the preceding year to assess the "big picture" by ensuring that routine quality actions taken and reviewed on a monthly basis are not components of larger systematic concerns. The monthly

review should keep the quality systems current and effective, therefore, the annual review is a formal senior management process to review specific existing documentation. Significant issues from the following documentation are compiled or summarized by the QA Manager prior to the review meeting:

- Matters arising from the previous annual review.
- Prior Monthly QA Reports issues.
- Laboratory QA Metrics.
- Review of report reissue requests.
- Review of client feedback and complaints.
- Issues arising from any prior management or staff meetings.
- Minutes from prior senior lab management team meetings. Issues that may be raised from these meetings include:
    - Adequacy of staff, equipment and facility resources.
    - Adequacy of policies and procedures.
    - Future plans for resources and testing capability and capacity.
- The annual internal double blind PT program sample performance (if performed),
- Compliance to the Ethics Policy and Data Integrity Plan. Including any evidence/incidents of inappropriate actions or vulnerabilities related to data Integrity.
- Evaluation of overall risk, including risks to impartiality, confidentiality, reporting statements of conformity, and nonconforming work.

A report is generated by the QA Manager and management staff. The report is distributed to the Laboratory Manager, President of the Business Unit and Business Unit Manager. The report includes, but is not limited to:

- The date of the review and the names and titles of participants.
- A reference to the existing data quality related documents and topics that were reviewed.
- Quality system or operational changes or improvements that will be made as a result of the review [e.g., an implementation schedule including assigned responsibilities for the changes (Action Table)].

Changes to the quality systems requiring update to the laboratory QA Manual shall be included in the next revision of the QA Manual.

18.3 POTENTIAL INTEGRITY RELATED MANAGERIAL REVIEWS

Potential integrity issues (data or business related) must be handled and reviewed in a confidential manner until such time as a follow-up evaluation, full investigation, or other appropriate actions have been completed and issues clarified. NDSC Document No. QA-SOP38228, Internal *Investigations* shall be followed. All investigations that result in finding of inappropriate activity are documented and include any disciplinary actions involved, corrective actions taken, and all appropriate notifications of clients.

The Eurofins Environment Testing America Presidents, Business Unit Managers, Laboratory Directors, NDSC Team are informed of any current data integrity or data recall investigations via the monthly metrics report.

SECTION 19

TEST METHODS AND METHOD VALIDATION

19.1 OVERVIEW

The laboratory uses methods that are appropriate to meet our clients' requirements and that are within the scope of the laboratory's capabilities. These include sampling, handling, transport, storage and preparation of samples, and, where appropriate, an estimation of the measurement of uncertainty as well as statistical techniques for analysis of environmental data.

Instructions are available in the laboratory for the operation of equipment as well as for the handling and preparation of samples. All instructions, Standard Operating Procedures (SOPs), reference methods and manuals relevant to the working of the laboratory are readily available to all staff. Deviations from published methods are documented (with justification) in the laboratory's approved SOPs. SOPs are submitted to clients for review at their request. Significant deviations from published methods require client approval and regulatory approval where applicable.

19.2 STANDARD OPERATING PROCEDURES (SOPs)

The laboratory maintains SOPs that accurately reflect all phases of the laboratory such as assessing data integrity, corrective actions, handling customer complaints as well as all analytical methods and sampling procedures. The method SOPs are derived from the most recently promulgated/approved, published methods and are specifically adapted to the laboratory facility. Modifications or clarifications to published methods are clearly noted in the SOPs. All SOPs are controlled in the laboratory:

- All SOPs contain a revision number, effective date, and appropriate approval signatures. Controlled copies are available to all staff.
- Procedures for preparation, review, revision and control are incorporated by reference to NDSC Document No. CED-Q-DC-SOP45894, Writing a Standard Operating Procedure, and the laboratory SOPs *UP-QA-032*, SOP Change Protocol and SOP *UP-QA-006*, Document Control.
- SOPs are reviewed on an annual basis and where necessary, revised to ensure continuing suitability and compliance with applicable requirements. The Eurofins Chicago SOP List (CHI-22-09-456) is used to document the current status of each SOP. This SOP list is updated in real-time, changing on a monthly basis and is available upon request.

19.3 LABORATORY METHODS MANUAL

For each test method, the laboratory shall have available the published referenced method as well as the laboratory developed SOP.

Note: If more stringent standards or requirements are included in a mandated test method or regulation than those specified in this manual, the laboratory shall demonstrate that such requirements are met. If it is not clear which requirements are more stringent, the standard from the method or regulation is to be followed. Any exceptions or deviations from the referenced methods or regulations are noted in the specific analytical SOP.

The laboratory maintains an SOP Index for both technical and non-technical SOPs. Technical SOPs are maintained to describe a specific test method. Non-technical SOPs are maintained to describe functions and processes not related to a specific test method.

19.4 SELECTION OF METHODS

Since numerous methods and analytical techniques are available, continued communication between the client and laboratory is imperative to assure the correct methods are utilized. Once client methodology requirements are established, this and other pertinent information is summarized by the PM. These mechanisms ensure that the proper analytical methods are applied when the samples arrive for log-in. For non-routine analytical services (e.g., special matrices, non-routine compound lists, etc.), the method of choice is selected based on client needs and available technology. The methods selected should be capable of measuring the specific parameter of interest, in the concentration range of interest, and with the required precision and accuracy.

19.4.1 Sources of Methods

Routine analytical services are performed using standard EPA-approved methodology. In some cases, modification of standard approved methods may be necessary to provide accurate analyses of particularly complex matrices. When the use of specific methods for sample analysis is mandated through project or regulatory requirements, only those methods shall be used.

When clients do not specify the method to be used or methods are not required, the methods used will be clearly validated and documented in an SOP and available to clients and/or the end user of the data. Refer to Appendix 3 for a list of the currently accepted U.S. EPA analytical method references used by the laboratory.

The laboratory reviews updated versions to all the aforementioned references for adaptation based upon capabilities, instrumentation, etc., and implements them as appropriate. As such, the laboratory strives to perform only the latest versions of each approved method as regulations allow or require.

Other reference procedures for non-routine analyses may include methods established by specific states (e.g., Underground Storage Tank methods), ASTM or equipment manufacturers. Sample type, source, and the governing regulatory agency requiring the analysis will determine the method utilized.

The laboratory shall inform the client when a method proposed by the client may be inappropriate or out of date. After the client has been informed, and they wish to proceed contrary to the laboratory's recommendation, it will be documented.

19.4.1.1 Client Supplied Methods

Most of the client-supplied method requirements presented to us involve achieving specific quality control criteria, limits of quantitation (LOQ), and/or method detection limits (MDL) using standard EPA methods. These requirements are communicated to the appropriate technical groups prior to the project start up. Each technical group evaluates the scope of work and the requirements to ensure the criteria can be met using the standard EPA method. The data is monitored to ensure the criteria are met throughout the project. The PM notifies the client if there is a more appropriate method available or if the client's criteria cannot be achieved on a certain sample matrix (i.e., due to matrix or dilutions).

Occasionally, we are asked to transfer a non-standardized method from a client into our lab or to develop a new method, when one is not available. In the case of a method transfer, we set up the client's method and perform some initial evaluation. After the initial evaluation, we may make recommendations on how to improve method performance. If the method appears to be adequate, we determine linearity, specificity, precision, accuracy, MDL, and LOQ by performing calibrations, analyzing method blanks, and carrying out method detection limit and IDOC studies.

In the case of method development, we work with the client and/or data user to determine the level of validation required ensuring that the method meets its intended purpose. In addition to the elements above, we also determine standard and sample stability and robustness depending on the scope of the project. Typically, a standard operating procedure is written and submitted to the client with the results of the validation. These steps are completed prior to analysis of field samples. Data related to the setup of the method are archived.

19.4.1.2 Procedural Deviations

Analysts are required to follow a documented method for all tests performed; and any deviations from analytical methods must be documented, approved, and justified in an appropriate and consistent manner. We classify method deviations as either being a planned deviation or an unplanned deviation. In general, the following information is captured to document both types of situations:

- Description of the situation
- Reason or justification for the deviation
- Impact the deviation had on the testing
- Signature/date of analyst performing the test
- Signature/date of QA and Laboratory management approving the deviation
- Signature/date of client approval, if necessary

Deviations to written procedures are documented in raw data records, ICAT or through the ICAR (Investigation and Corrective Action Report) system. Both types of documentation require management and QA review and approval.

NOTE: Deviations to analytical methods are not permitted by PALA. If samples are analyzed for compliance to a regulatory program, deviations may be allowed with approval from the appropriate compliance officer and/or program.

19.4.2 Demonstration of Capability

Before the laboratory may institute a new method and begin reporting results, the laboratory shall confirm that it can properly operate the method. In general, this demonstration does not test the performance of the method in real world samples, but in an applicable and available clean matrix sample. If the method is for the testing of analytes that are not conducive to spiking, demonstration of capability may be performed on quality control samples.

19.4.2.1 A demonstration of capability (DOC, Laboratory SOP UP-QA-014) is performed whenever there is a change in instrument type (e.g., new instrumentation), matrix, method or personnel (e.g., analyst hasn't performed the test within the last 12 months). A continuing demonstration of capability (CDOC) study is required on an annual basis.

Note: The laboratory shall have a DOC for all analytes included in the methods that the laboratory performs, and proficiency DOCs for each analyst shall include all analytes that the laboratory routinely performs. Addition of non-routine analytes does not require new DOCs for all analysts if those analysts are already qualified for routine analytes tested using identical chemistry and instrument conditions.

19.4.2.2 The initial demonstration of capability must be thoroughly documented and approved by the Technical Manager and QA Manager prior to independently analyzing client samples. All associated documentation must be retained in accordance with the laboratories archiving procedures (refer to Section 16, Control of Records).

19.4.2.3 The laboratory must have an approved SOP, demonstrate satisfactory performance, and conduct a method detection limit study (when applicable). There may be other requirements as stated within the published method or regulations (i.e., retention time window study).

Note: In some instances, a situation may arise where a client requests that an unusual analyte be reported using a method where this analyte is not normally reported. If the analyte is being reported for regulatory purposes, the method must meet all procedures outlined within this QA Manual (SOP, MDL, and Demonstration of Capability). If the client states that the information is not for regulatory purposes, the result may be reported as long as the following criteria are met:

- The instrument is calibrated for the analyte to be reported using the criteria for the method and ICV/CCV criteria are met (unless an ICV/CCV is not required by the method or criteria are per project DQOs).
- The laboratory's nominal or default reporting limit (RL) is equal to the Limit of Quantitation (LOQ), which must be at or above the lowest non-zero standard in the calibration curve and achieve an adequate level of precision and bias. Project RLs are client specified reporting levels which may be higher than the QL. Results reported below the LOQ must be qualified as estimated values. Also see Section 19.6.1.3, Relationship of Limit of Detection (LOD) to Limit of Quantitation (LOQ).
- The client request is documented and the lab informs the client of its procedure for working with unusual compounds. The final report must be footnoted and or narrated: *Reporting Limit (RL) or the Limit of Quantitation (LOQ) is based on the low standard of the calibration curve.*

19.4.3 Initial Demonstration of Capability (IDOC) Procedures

19.4.3.1 The spiking standard used must be prepared independently from those used in instrument calibration.

19.4.3.2 The analyte(s) shall be diluted in a volume of clean matrix sufficient to prepare four aliquots at the concentration specified by a method or the laboratory SOP. The laboratory will utilize the 'split and spike' procedure, i.e., a clean water or soil matrix shall be split into four portions first and then each portion is individually spiked.

19.4.3.3 At least four aliquots shall be prepared (including any applicable clean-up procedures) and analyzed according to the test method (either concurrently or over a period of several days).

19.4.3.4 Using all of the results, calculate the mean recovery in the appropriate reporting units and the standard deviations for each parameter of interest.

19.4.3.5 When it is not possible to determine the mean and standard deviations, such as for presence, absence and logarithmic values, the laboratory will assess performance against criteria described in the Method SOP.

19.4.3.6 Compare the information obtained above to the corresponding acceptance criteria for precision and accuracy in the test method (if applicable) or in laboratory generated acceptance criteria (LCS or interim criteria) if there is no mandatory criteria established. If any one of the parameters do not meet the acceptance criteria, the performance is unacceptable for that parameter.

19.4.3.7 When one or more of the tested parameters fail at least one of the acceptance criteria, the analyst must proceed according to either option listed below:

- Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with 19.4.3.3 above.
- Beginning with 19.4.3.3 above, repeat the test for all parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with 19.4.3.1 above.

Note: Results of successive LCS analyses can be used to fulfill the DOC requirement.

Methods on line prior to the effective date of this Section shall be updated to the procedures outlined above as new analysts perform their demonstration of capability. A copy of the new record will replace that which was used for documentation in the past. At a minimum, the precision and accuracy of four mid-level laboratory control samples must have been compared to the laboratory's quality control acceptance limits.

19.5 LABORATORY DEVELOPED METHODS AND NON-STANDARD METHODS

Any new method developed by the laboratory must be fully defined in an SOP and validated by qualified personnel with adequate resources to perform the method. Method specifications and the relation to client requirements must be clearly conveyed to the client if the method is a non-standard method (not a published or routinely accepted method). The client must also be in agreement to the use of the non-standard method.

19.6 VALIDATION OF METHODS

Validation is the confirmation by examination and the provision of objective evidence that the particular requirements for a specific intended use are fulfilled.

All non-standard methods, laboratory designed/developed methods, standard methods used outside of their scope, and major modifications to published methods must be validated to confirm they are fit for their intended use. The validation will be as extensive as necessary to meet the needs of the given application. The results are documented with the validation procedure used and contain a statement as to the fitness for use.

19.6.1 Method Validation and Verification Activities for All New Methods

While method validation can take various courses, the following activities can be required as part of method validation. Method validation records are designated QC records and are archived accordingly.
When changes are made to any validated methods, the influence of such changes shall be documented and, if appropriate, a new validation shall be performed.

19.6.1.1 Determination of Method Selectivity

Method selectivity is the demonstrated ability to discriminate the analyte(s) of interest from other compounds in the specific matrix or matrices from other analytes or interference. In some cases to achieve the required selectivity for an analyte, a confirmation analysis is required as part of the method.

19.6.1.2 Determination of Method Sensitivity

Sensitivity can be both estimated and demonstrated. Whether a study is required to estimate sensitivity depends on the level of method development required when applying a particular measurement system to a specific set of samples. Detection limit studies are conducted as described in Section 19.7 below. Where other protocols for estimations and/or demonstrations of sensitivity are required by regulation or client agreement, these shall be followed.

19.6.1.3 Relationship of Limit of Detection (LOD) to the Limit of Quantitation (LOQ)

An important characteristic of expression of sensitivity is the distinction between the LOD and the LOQ. The LOD is the minimum level at which the presence of an analyte can be reliably concluded. The LOQ is the minimum concentration of analyte that can be quantitatively determined with acceptable precision and bias, equivalent to the laboratory's routine reporting limit (RL). For most instrumental measurement systems, there is a region where semi-quantitative data is generated around the LOD (both above and below the estimated MDL or LOD) and below the LOQ. In this region, detection of an analyte may be confirmed but quantification of the analyte is unreliable within the accuracy and precision guidelines of the measurement system. When an analyte is detected below the LOQ, and the presence of the analyte is confirmed by meeting the qualitative identification criteria for the analyte, the analyte can be reliably reported, but the amount of the analyte can only be estimated. If data is to be reported in this region, it must be done so with a qualification that denotes the semi-quantitative nature of the result.

19.6.1.4 Determination of Interferences

A determination that the method is free from interferences in a blank matrix is performed.

19.6.1.5 Determination of Range

Where appropriate to the method, the quantitation range is determined by comparison of the response of an analyte in a curve to established or targeted criteria. Generally the upper quantitation limit is defined by the highest acceptable calibration concentration. The lower quantitation limit or QL cannot be lower than the lowest non-zero calibration level, and can be constrained by required levels of bias and precision.

19.6.1.6 Determination of Accuracy and Precision

Accuracy and precision studies are generally performed using replicate analyses, with a resulting percent recovery and measure of reproducibility (standard deviation, relative standard deviation) calculated and measured against a set of target criteria.

19.6.1.7 Documentation of Method

The method is formally documented in an SOP. If the method is a minor modification of a standard laboratory method that is already documented in an SOP, an SOP Attachment describing the specific differences in the new method is acceptable in place of a separate SOP.

19.6.1.8 Continued Demonstration of Method Performance

Continued demonstration of Method Performance is addressed in the SOP. Continued demonstration of method performance is generally accomplished by batch specific QC samples such as LCS, method blanks or PT samples.

19.7 METHOD DETECTION LIMITS (MDL)/ LIMITS OF DETECTION (LOD)

The Method detection limit (MDL) is the minimum measured quantity of a substance that can be reported with 99% confidence that the concentration is distinguishable from method blank results, consistent with 40 CFR Part 136, Appendix B, August 2017. The MDL is equivalent to the TNI LOD, and is also equivalent to the DoD/DOE Quality Systems Manual (QSM) DL. The working or final MDL is the higher of the MDL value determined from spikes (MDLs) and the MDL determined from blanks (MDLb). An initial MDL shall be performed during the method validation process and when the method is altered in a way that can reasonably be expected to change its sensitivity. On-going data are collected during each quarter in which samples are being analyzed. At least

once every 13 months the MDLs and MDLb are re-calculated and re-evaluated using data collected during the preceeding period. Details of the laboratory's procedure for conducting MDL studies are given in NDSC Document No. NDSC-QA-SOP42091 and the laboratory SOP UP-QA-017, Method Detection Limits (MDL).

19.7.1 MDLs are initially performed for each individual instrument and non-microbiological method analysis. The laboratory will pool the data to calculate the MDL for all instruments used for a given method as the MDL for reporting purposes. This MDL is not required for methods that are not readily spiked (e.g. pH, turbidity, etc.) or where the lab does not report values to the MDL. Titration and gravimetric methods where there is no additional preparation involved, the MDL is based on the lowest discernable unit of measure that can be observed.

19.7.2 MDLs must be run against acceptable instrument QC, including ICV's and Tunes as per the requirement of the method that is being analyzed. This is to insure that the instrument is in proper working condition and falsely high or low MDLs are not calculated.

19.7.3 Use only clean matrix which is free of target analytes (e.g.: Laboratory reagent water, Ottawa Sand) unless a project specific MDL is required in a field sample matrix.

19.7.4 Each of the spikes must be qualitatively identifiable (e.g., appear in both columns for dual column methods, characteristic ions for GCMS mass spectra, etc). Manual integrations to force the baseline for detection are not allowed.

19.7.5 The initial MDL is calculated as follows:

$MDL = t_{(n-1,\ 1-a\ =\ 0.99)}$ x (Standard Deviation of replicates)

where $t_{(n-1,\ 1-a\ =\ 0.99)}$ = 3.143 for seven replicates.
where $t_{(n-1,\ 1-a\ =\ 0.99)}$ = 2.998 for eight replicates.

19.7.6 Because of the inherent variability in results outside of the calibration range, the laboratory does not recommend the reporting of results below the lowest calibration point in a curve; however, it is recognized that some projects and agencies require the reporting of results below the RL/LOQ. Any result that falls between the MDL/LOD and the RL/LOQ, when reported, will be qualified as an estimated value.

19.7.7 MDLs/LODs and RLs/LOQs are adjusted in LIMs based on moisture content and sample aliquot size.

19.8 VERIFICATION OF DETECTION LIMITS

If it is found during the re-evaluation of detection limit results that more than 5% of the spiked samples do not return positive numeric results that meet all method qualitative identification criteria, then the spiking level shall be increased and the initial MDL study pre-performed at the new spiking concentration.

19.9 Instrument Detection Limits (IDL)

The IDL is sometimes used to assess the reasonableness of the MDL or in some cases required by the analytical method or program requirements. IDLs are most commonly used in metals analyses but may be useful in demonstration of instrument performance in other areas.

IDLs are calculated to determine an instrument's sensitivity independent of any preparation method. IDLs are calculated either using 7 replicate spike analyses, like MDL but without sample preparation, or by the analysis of 10 instrument blanks and calculating 3 x the absolute value of the standard deviation.

19.10 Limit of Quantitation (LOQ)

The LOQ shall be at a concentration equivalent to the lowest calibration standard concentration, with the exception of methods using a single-point calibration, and shall be greater than the MDL. The LOQ is verified by preparing and analyzing spikes at concentrations 1-2 times the selected LOQ, employing the complete analytical process.

When the laboratory establishes a quantitation limit, it must be initially verified by the analysis of a low level standard or QC sample at 1-2 times the reporting limit or by a DL check sample at or below the LOQ. The LOQ is verified annually thereafter. The annual requirement is waived for methods that have an annually verified MDL. The laboratory will comply with any regulatory requirements.

The acceptance criteria of +/- 30% of the mean will be applied except for those poor performers that are identified in the specific methods and/or SOPs. The QC standard will be designated in TALs as a Method Reporting Limit check standard (MRL). There are method, program or state requirements that specify the running and reporting of the method reporting limit check standard in sequence with the analytical runs associated with their samples. This special project requirement is communicated to the laboratory via project and Job login notes.

19.11 RETENTION TIME WINDOWS

Most organic analyses and some inorganic analyses use chromatography techniques for qualitative and quantitative determinations. For every chromatography analysis each analyte will have a specific time of elution from the column to the detector. This is known as the analyte's retention time. The variance in the expected time of elution is defined as the retention time window. As the key to analyte identification in chromatography, retention time windows must be established on every column for every analyte used for that method as specified in the reference method. These records are kept on-file and available for review. Complete details are available in the laboratory SOPs.

19.12 EVALUATION OF SELECTIVITY

The laboratory evaluates selectivity by following the checks within the applicable analytical methods, which include mass spectral tuning, second column confirmation, ICP interelement interference checks, chromatography retention time windows, sample blanks, spectrochemical, atomic absorption or fluorescence profiles, co-precipitation evaluations and specific electrode response factors.

19.13 ESTIMATION OF UNCERTAINTY OF MEASUREMENT

19.13.1 Uncertainty is "a parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand" (as defined by the International Vocabulary of Basic and General Terms in Metrology, ISO Geneva, 1993, ISBN 92-67-10175-1). Knowledge of the uncertainty of a measurement provides additional confidence in a result's validity. Its value accounts for all the factors which could possibly affect the result, such as adequacy of analyte definition, sampling, matrix effects and interferences, climatic conditions, variances in weights, volumes, and standards, analytical procedure, and random variation. Some national accreditation organizations require the use of an "expanded uncertainty": defined as the range within which the value of the measurand is believed to lie within at least a 95% confidence level with the coverage factor k=2.

19.13.2 Uncertainty is not error. Error is a single value, (i.e., the difference between the true result and the measured result). On environmental samples, the true result is never known. The measurement is the sum of the unknown true value and the unknown error. Unknown error

is a combination of systematic error, or bias, and random error. Bias varies predictably, constantly, and independently from the number of measurements. Random error is unpredictable, assumed to be Gaussian in distribution, and reducible by increasing the number of measurements.

19.13.3 The minimum uncertainty associated with results generated by the laboratory can be determined by using the Laboratory Control Sample (LCS) accuracy range for a given analyte. The LCS limits are used to assess the performance of the measurement system since they take into consideration all of the laboratory variables associated with a given test over time (except for variability associated with the sub sampling and the variability due to matrix effects). The percent recovery of the LCS is compared either to the method-required LCS accuracy limits or to the statistical, historical, in-house LCS accuracy limits.

19.13.4 To calculate the uncertainty for the specific result reported, multiply the result by the decimal of the lower end of the LCS range percent value for the lower end of the uncertainty range, and multiply the result by the decimal of the upper end of the LCS range percent value for the upper end of the uncertainty range. These calculated values represent uncertainties at approximately the 99% confidence level with a coverage factor k = 3. As an example, for a reported result of 1.0 mg/l with an LCS recovery range of 50 to 150%, the estimated uncertainty in the result would be 1.0 +/- 0.5 mg/L. Refer to the laboratory's SOP *UP-QA-040*, Quality Assurance – Measurement Uncertainty for additional details.

19.13.5 In the case where a well-recognized test method specifies limits to the values of major sources of uncertainty of measurement (e.g. 524.2, 525, etc) and specifies the form of presentation of calculated results, no further discussion of uncertainty is required.

19.14 SAMPLE REANALYSIS GUIDELINES

Because there is a certain level of uncertainty with any analytical measurement, a sample re-preparation (where applicable) and subsequent analysis (hereafter referred to as 'reanalysis') may result in either a higher or lower value from an initial sample analysis. There are also variables that may be present (e.g., sample homogeneity, analyte precipitation over time, etc.) that may affect the results of a reanalysis. Based on the above comments, the laboratory will reanalyze samples at a client's request with the following caveats. **Client specific Contractual Terms & Conditions for reanalysis protocols may supercede the following items.**

- Homogenous samples: If a reanalysis agrees with the original result to within the RPD limits for MS/MSD or Duplicate analyses, or within $\pm$ 1 reporting limit for samples $\leq$ 5x the reporting limit, the original analysis will be reported. At the client's request, both results may be reported on the same report but not on two separate reports.
- If the reanalysis does not agree (as defined above) with the original result, then the laboratory will investigate the discrepancy and reanalyze the sample a third time for confirmation if sufficient sample is available.
- Any potential charges related to reanalysis are discussed in the contract terms and conditions or discussed at the time of the request. The client will typically be charged for reanalysis unless it is determined that the lab was in error.
- Due to the potential for increased variability, reanalysis may not be applicable to Non-homogenous, Encore, and Sodium Bisulfate preserved samples. See the Area Supervisor/Manager or Laboratory Director if unsure.

19.15 CONTROL OF DATA

The laboratory has policies and procedures in place to ensure the authenticity, integrity, and accuracy of the analytical data generated by the laboratory.

19.15.1 Computer and Electronic Data Related Requirements

The three basic objectives of our computer security procedures and policies are shown below.

The laboratory is currently using the Eurofins LIMS system, which has been highly customized to meet the needs of the laboratory.

19.15.1.1 Maintain the Database Integrity: Assurance that data is reliable and accurate through data verification (review) procedures, password-protecting access, anti-virus protection, data change requirements, as well as an internal LIMS permissions procedure.

- LIMS Database Integrity is achieved through data input validation, internal user controls, documentation of system failures and corrective actions taken, and data change requirements.
- Spreadsheets and other software developed in-house must be verified with documentation through hand calculations prior to use. Cells containing calculations must be lock-protected and controlled.
- Instrument hardware and software adjustments are safeguarded through maintenance logs, audit trails and controlled access.

19.15.1.2 Ensure Information Availability: Protection against loss of information or service through scheduled back-ups, stable file server network architecture, secure storage of media, line filter, Uninterruptible Power Supply (UPS), and maintaining older versions of software as revisions are implemented.

19.15.1.3 Maintain Confidentiality: Ensure data confidentiality through physical access controls such as password protection or website access approval, when electronically transmitting data.

19.15.2 Data Reduction

The complexity of the data reduction depends on the analytical method and the number of discrete operations involved (e.g., extractions, dilutions, instrument readings and concentrations). The analyst calculates the final results from the raw data or uses appropriate computer programs to assist in the calculation of final reportable values. Calculations are independently verified by appropriate laboratory staff. Calculations and data reduction steps for various methods are summarized in the respective analytical SOPs or program requirements.

For manual data entry, e.g., Wet Chemistry, the data is reduced by the analyst and then verified by the Department Manager, Supervisor or alternate analyst prior to updating the data in TALs. The spreadsheets, or any other type of applicable documents, are signed by both the analyst and alternate reviewer to confirm the accuracy of the manual entry(s).

Manual integration of peaks will be documented and reviewed and the raw data will be flagged in accordance with the NDSC Document No. NDSC-QA-SOP43862, *Manual Integrations*.

Analytical results are reduced to appropriate concentration units specified by the analytical method, taking into account factors such as dilution, sample weight or volume, etc. Blank correction will be applied only when required by the method or per manufacturer's indication; otherwise, it should not be performed. Calculations are independently verified by appropriate laboratory staff. Calculations and data reduction steps for various methods are summarized in the respective analytical SOPs or program requirements.

19.15.2.1 All raw data must be retained in the worklist folder, computer file (if appropriate), and/or runlog. All criteria pertinent to the method must be recorded. Raw data must include all pertinent information needed to reconstruct the final result from the bench notes or instrument file reported value, and accurately reflect the method used, instrument ID, analyst, and time of preparation and analysis. It may include annotated instrument hard-copies, bench notes, completed bound data book pages, or pages printed directly from the LIMS. The documentation is recorded at the time observations or calculations are made and must be signed or initialed/dated (month/day/year). It must be easily identifiable who performed which tasks if multiple people were involved.

19.15.2.2 In general, concentration results are reported in milligrams per liter (mg/L) or micrograms per liter (µg/L) for liquids and milligrams per kilogram (mg/kg) or micrograms per kilogram (µg/kg) for solids. For values greater than 10,000 mg/L, results can be reported in percent, i.e., 10,000 mg/L = 1**%.** Default reporting units are defined in each laboratory SOP and in the analytical method setup in LIMS.

19.15.2.3 In reporting, the analyst or the instrument output records the raw data result using values of known certainty plus one uncertain digit. If final calculations are performed external to LIMS, the results should be entered in LIMS with at least three significant figures. In general, results are reported to 2 significant figures on the final report.

19.15.2.4 For those methods that do not have an instrument printout or an instrumental output compatible with the LIMS, the raw results and dilution factors are entered directly into LIMS by the analyst, and the software calculates the final result for the analytical report. LIMS has a formatter for significant figure criterion for each analyte.

19.15.2.5 The laboratory strives to import data directly from instruments or calculation spreadsheets to ensure that the reported data are free from transcription and calculation errors. For those analyses with an instrumental output compatible with the LIMS, the raw results and dilution factors are transferred into LIMS electronically after the initial data review has been performed by the analyst according to review procedures identified in the individual laboratory SOPs. (For example, included in the organics data review is the evaluation of the Chrom data system's quantitation report/spectra for each sample and analyte, actions such as removing unrequested or poor spectrally-matched compounds may be necessary prior to data import into LIMS). Depending on the data to be reviewed, the analyst either prints a copy or views the data on screen to check for errors in accordance with the laboratory's analytical SOPs and data review checklists. Secondary review of the data is done and recorded on the same checklist by a peer reviewer or supervisor. The raw data, including the checklist, instrument print-outs, and manual entries, and electronic files are retained for easy retrieval in accordance with the laboratory's record and retention policy outlined in Section 16.6.

19.15.3 Logbook / Worksheet Use Guidelines

Logbooks and worksheets are filled out 'real time' and have enough information on them to trace the events of the applicable analysis/task. (e.g. calibrations, standards, analyst, sample ID, date, time on short holding time tests, temperatures when applicable, calculations are traceable, etc.)

- Corrections are made following the procedures outlined in Section 14.
- Logbooks are controlled by the QA department. A record is maintained of all logbooks in the lab.
- Unused portions of pages must be "Z"'d out, signed and dated.
- Worksheets are created with the approval of the Technical Manager, Operations Manager, Department Supervisor and QA Manager at the facility. The QA Manager controls all worksheets following the procedures in Section 8.

19.15.4 Review / Verification Procedures

Review procedures are out lined in several SOPs [e.g. Sample Control, Project Management, QA and Method Specific SOPs] to ensure that reported data are free from calculation and transcription errors, that QC parameters have been reviewed and evaluated before data is reported. The laboratory also follows the NDSC Document No. NDSC-QA-SOP43862, Manual Integrations, to ensure the authenticity of the data. The general review concepts are discussed below, more specific information can be found in the laboratory SOPs.

19.15.4.1 Log-In Review

The data review process starts at sample receipt stage. Sample control personnel review chain-of-custody forms and project instructions from the project management group. This is the basis of the sample information and analytical instructions entered into the LIMS. The log-in instructions are reviewed by the personnel entering the information, and a second level review is conducted by the project management staff.

19.15.4.2 First Level Data Review

The next level of data review occurs with the analysts. As data are generated, analysts review their work to ensure that the results meet project and SOP requirements. First level reviews include inspection of all raw data (e.g., instrument output for continuous analyzers, chromatograms, spectra, and manual integrations), evaluation of calibration/calibration verification data in the day's analytical run, evaluation of QC data, and reliability of sample results. The analysts transfer the data into the LIMS, data qualifiers are added as needed. Where non-compliance is observed, the analyst creates Non-Conformance Memos (NCMs) in LIMS (see Appendix 7 for list of default data qualifiers). The project manager selects a formatter in LIMS that will be assigned to the project and any login associated with the project. The flags and qualifiers are then automatically applied to the data when calculated and is reviewed by the analyst as part of the data review process. All first level reviews are documented on a LIMS electronic Checklist in the AD Batch or on a paper data review checklist if the electronic checklist is not available for the method. After the review is complete, the batch status in LIMS is set to 1st level review.

19.15.4.3 Second Level Data Review

All analytical data are subject to review by a second qualified analyst or supervisor. Second level reviews include inspection of all raw data (e.g., instrument output, chromatograms, and spectra) including 100% of data associated with any changes made by the primary analyst, such as manual integrations or reassignment of peaks to different analytes, or elimination of false negative analytes. The second review also includes evaluation of initial calibration/calibration verification data in the day's analytical run, evaluation of QC data, reliability of sample results, qualifiers and NCM narratives. Manual calculations are checked in second level review. After the review is complete, the batch status is then set to 2nd level review. All second level reviews are documented using the same checklist as the 1st level reviewer.

Issues that deem further review include the following:

- QC data are outside the specified control limits for accuracy and precision
- Reviewed sample data does not match with reported results
- Unusual detection limit changes are observed
- Samples having unusually high results
- Samples exceeding a known regulatory limit
- Raw data indicating some type of contamination or poor technique
- Inconsistent peak integration
- Transcription errors
- Results outside of calibration range

19.15.4.4 Unacceptable analytical results may require reanalysis of the samples. Any problems are brought to the attention of the Laboratory Director, Project Manager, Quality Director/Manager, Technical Manager, or Supervisor for further investigation. Corrective action is initiated whenever necessary.

19.15.4.5 The results are then entered or directly transferred into the computer database and a .pdf is printed for the client.

19.15.4.6 As a final review prior to the release of the report, the Project Manager reviews the results for appropriateness and completeness. This review and approval ensures that client requirements have been met and that the final report has been properly completed. This process includes, but is not limited to, verifying that the COC is followed, cover letters / narratives are present, flags are appropriate, and project specific requirements are met. The Project Manager may also evaluate the validity of results for different test methods given expected chemical relationships.

19.15.4.7 When all the individual tests for a department are at 2nd level review for a job, the Supervisor or the Supervisor's designee reviews the entire job, comparing chemical relationships, reviewing for completeness and the presence of appropriate NCMs, and doing an overall evaluation of the results summary.

Examples of chemical relationships evaluated by the supervisor prior to setting data to 'Lab Complete' status include the following:

- Total Results are ≥ Dissolved results (e.g. metals)
- Total Solids (TS) ≥ TDS or TSS
- TKN ≥ Ammonia
- Total Phosphorus ≥ Orthophosphate
- COD ≥ BOD
- Total Cyanide ≥ Amenable Cyanide
- TDS ≥ individual anions

19.15.4.8 Any project that requires a data package is subject to a tertiary data review for transcription errors and acceptable quality control requirements prior to setting the job to a 'Lab Complete' status. The data management staff assembles the preliminary report for the PM or their designee. As a final review prior to the release of the report, the PM or designee reviews the results for appropriateness and completeness. This review and approval ensures that client requirements have been met and that the final report has been properly completed. The process includes, but is not limited to, verifying that the COC is followed, cover letters / narratives are present and that flags are appropriate. The PM will also check for invoicing errors prior to its approval. When complete, the report is sent out to the client.

19.15.4.9 A brief overview of flows and information through the laboratory, as well as data review and validation, is presented in Figure 19-1.

19.15.5 Manual Integrations

Computerized data systems provide the analyst with the ability to re-integrate raw instrument data in order to optimize the interpretation of the data. Though manual integration of data is an invaluable tool for resolving variations in instrument performance and some sample matrix problems, when used improperly, this technique would make unacceptable data appear to meet quality control acceptance limits. Improper re-integrations lead to legally indefensible data, a poor reputation, or possible laboratory decertification. Because guidelines for re-integration of data are not provided in the methods and most methods were written prior to widespread implementation of computerized data systems, the laboratory trains all analytical staff on proper manual integration techniques using NDSC Document No. NDSC-QA-SOP43862, Manual Integrations, as the guidelines for laboratory's analysis.

19.15.5.1 The analyst must adjust baseline or the area of a peak in some situations, for example when two compounds are not adequately resolved or when a peak shoulder needs to be separated from the peak of interest. The analyst must use professional judgment to determine when manual integrating is required. Analysts are encouraged to ask for assistance from a senior analyst or manager when in doubt.

19.15.5.2 Analysts shall not increase or decrease peak areas to for the sole purpose of achieving acceptable QC recoveries that would have otherwise been unacceptable. The intentional recording or reporting of incorrect information (or the intentional omission of correct information) is against company principals and policy and is grounds for immediate termination.

19.15.5.3 Client samples, performance evaluation samples, and quality control samples are all treated equally when determining whether or not a peak area or baseline should be manually adjusted.

19.15.5.4 All manual integrations receive a second level review. Manual integrations must be indicated on an expanded scale “after” chromatograms such that the integration performed can be easily evaluated during data review. Expanded scale “before” chromatograms are also required for all manual integrations on QC parameters (calibrations, calibration verifications, laboratory control samples, internal standards, surrogates, etc.) unless the laboratory has another documented NDSC approved procedure in place that can demonstrate an active process for detection and deterrence of improper integration practices.

Figure 19-1 Eurofins Chicago Work Flow

Action	Personnel Involved
Bottle orders generated upon request - Bottles packed and shipped to the client under CoC	- Client Service Personnel / PM - Bottle Preparation Personnel
Samples received at laboratory - Unpacked and reconciled against client paperwork or CoC - Samples acceptance documented against completed (CoC)[1]	Sample Login Personnel
Samples are entered into LIMS - Job # assigned - Methods/Analytes linked from project - Sample labels generated - LIMS backlogs updated immediately	Sample Login Personnel
Sample Storage - Short TATs and hold-time samples are delivered directly to the laboratory for analysis - Samples stored in assigned locations (refrigerated walk-in coolers, freezers, VOA refrigerators; etc.)	Sample Login Personnel
Sample Receipt Acknowledgement sent to client (when requested)	Sample Login Personnel
Sample Acquisition/Testing - Analysts collect samples from assigned storage. - Legal CoC samples are signed in-and-out of storage - Remaining sample returned to storage.	Analysts / Login Personnel
Preparation and analysis is performed according to selected analytical method and applicable Project notes - Raw data recorded/reviewed[2] - Data imported to LIMS	Analysts
LIMS performs calculations: - Data reviewed by primary/secondary analyst - Data approved as final	Data Process (LIMS / Analyst)
Generation/review/release of reports (automated through LIMS) - Electronic copy saved in LIMS	Project Management Assistants / Reporting Group
Electronic Data Deliverables (EDDs) generated (as applicable)	EDD Group
Hard copy and electronic batch raw data is archived according to data archiving procedures.	Analysts / IT

[1]Refer to Sec. 23.3.
[2]Analyses requiring the analyst’s interpretation may involve manual data reduction before entry into LIMS.

SECTION 20

EQUIPMENT AND CALIBRATIONS

20.1 OVERVIEW

The laboratory purchases the most technically advanced analytical instrumentation for sample analyses. Instrumentation is purchased on the basis of accuracy, dependability, efficiency and sensitivity. Each laboratory is furnished with all items of sampling, preparation, analytical testing and measurement equipment necessary to correctly perform the tests for which the laboratory has capabilities. Each piece of equipment is capable of achieving the required accuracy and complies with specifications relevant to the method being performed. Before being placed into use, the equipment (including sampling equipment) is calibrated and checked to establish that it meets its intended specification. The calibration routines for analytical instruments establish the range of quantitation. Calibration procedures are specified in laboratory SOPs, the laboratory default criteria are summarized in the laboratory SOPs and in Appendix 4. A list of laboratory equipment and instrumentation is presented in Table 20-1.

Equipment is only operated by authorized and trained personnel. Manufacturer's instructions for equipment use are readily accessible to all appropriate laboratory personnel.

20.2 PREVENTIVE MAINTENANCE

20.2.1 The laboratory follows a well-defined maintenance program to ensure proper equipment operation and to prevent the failure of laboratory equipment or instrumentation during use. This program of preventive maintenance helps to avoid delays due to instrument failure.

20.2.2 Routine preventive maintenance procedures and frequency, such as lubrication, cleaning, and replacements, should be performed according to the procedures outlined in the manufacturer's manual. Qualified personnel must also perform maintenance when there is evidence of degradation of peak resolution, a shift in the calibration curve, loss of sensitivity, or failure to continually meet one of the quality control criteria.

20.2.3 Scheduled routine maintenance is defined in each method SOP. It is the responsibility of each Technical Manager to ensure that instrument maintenance logs are kept for all equipment in his/her department. Preventative maintenance procedures are also outlined in analytical SOPs or instrument manuals. (Note: for some equipment, the log used to monitor performance is also the maintenance log. Multiple pieces of equipment may share the same log as long as it is clear as to which instrument is associated with an entry.)

20.2.4 Instrument maintenance logs are controlled and are used to document instrument problems, instrument repair and maintenance activities. Maintenance logs shall be kept for all major pieces of equipment. Instrument maintenance logs may also be used to specify instrument parameters.

20.2.4.1 Documentation must include all major maintenance activities such as contracted preventive maintenance and service and in-house activities such as the replacement of electrical components, lamps, tubing, valves, columns, detectors, cleaning and adjustments.

20.2.4.2 Each entry in the instrument log includes the Analyst's initials, the date, a detailed description of the problem (or maintenance needed/scheduled), a detailed explanation of the solution or maintenance performed, and a verification that the equipment is functioning properly (state what was used to determine a return to control. e.g. CCV run on *'date'* was acceptable, or instrument recalibrated on 'date' with acceptable verification, etc.) must also be documented in the instrument records.

20.2.4.3 When maintenance or repair is performed by an outside agency, service receipts detailing the service performed can be affixed into the logbooks adjacent to pages describing the maintenance performed. This stapled in page must be signed across the page entered and the logbook so that it is clear that a page is missing if only half a signature is found in the logbook.

20.2.5 If an instrument requires repair (subjected to overloading or mishandling, gives suspect results, or otherwise has shown to be defective or outside of specified limits) it shall be taken out of operation and tagged as out of service or otherwise isolated until such a time as the repairs have been made and the instrument can be demonstrated as operational by calibration and/or verification or other test to demonstrate acceptable performance. The laboratory shall examine the effect of this defect on previous analyses (refer to Sections 13 and 14).

20.2.6 In the event of equipment malfunction that cannot be resolved, service shall be obtained from the instrument vendor manufacturer, or qualified service technician, if such a service can be tendered. If on-site service is unavailable, arrangements shall be made to have the instrument shipped back to the manufacturer for repair. Back up instruments, which have been approved, for the analysis shall perform the analysis normally carried out by the malfunctioning instrument. If the backup is not available and the analysis cannot be carried out within the needed timeframe, the samples shall be subcontracted using the procedures outlined in Section 10.

20.2.7 At a minimum, if an instrument is sent out for service or transferred to another facility, it must be recalibrated and the laboratory MDL verified (using an MDLV) prior to return to lab operations.

20.3 SUPPORT EQUIPMENT

This section applies to all devices that may not be the actual test instrument, but are necessary to support laboratory operations. These include but are not limited to: balances, ovens, refrigerators, freezers, incubators, water baths, field sampling devices, temperature measuring devices, thermal/pressure sample preparation devices and volumetric dispensing devices if quantitative results are dependent on their accuracy, as in standard preparation and dispensing or dilution into a specified volume. All raw data records associated with the support equipment are retained to document instrument performance.

20.3.1 Weights and Balances

The accuracy of the balances used in the laboratory is checked every working day, before use. All balances are placed on stable counter tops.

Each balance is checked prior to initial serviceable use with at least two certified ASTM Class 1 weights spanning its range of use (weights that have been calibrated to ASTM Class 1 weights may also be used for daily verification). ASTM Class 1 weights used only for calibration of other weights (and no other purpose) are inspected for corrosion, damage or nicks at least annually and if no damage is observed, they are calibrated at least every 5 years by an outside calibration laboratory. Any weights (including ASTM Class 1) used for daily balance checks or other purposes are recalibrated/recertified annually to NIST standards (this may be done internally if laboratory maintains “calibration only” ASTM Class 1 weights).

All balances are serviced annually by a qualified service representative, who supplies the laboratory with a certificate that identifies traceability of the calibration to the NIST standards.

All of this information is recorded in logs, and the recalibration/recertification certificates are kept on file. Refer to laboratory SOP UP-QA-003, *Balance Calibration Care and Use* for additional details.

20.3.2 pH, Conductivity, and Turbidity Meters

The pH meters used in the laboratory are accurate to ± 0.1 pH units, and have a scale readability of at least 0.05 pH units. The meters automatically compensate for the temperature, and are calibrated with at least two working range buffer solutions before each use, the ATC probes are verified annually.

Conductivity meters are also calibrated before each use with a known standard to demonstrate the meters do not exceed an error of 1% or one umhos/cm, whichever is greater. The meters are also calibrated before each use with a known standard.

Turbidity meters are also calibrated before each use. All of this information is documented in logs.

Consult pH and Conductivity, and Turbidity SOPs for further information.

20.3.3 Thermometers

All thermometers are calibrated on an annual basis with a NIST-traceable thermometer.

- If the temperature measuring device is used over a range of 10°C or less, then a single point verification within the range of use is acceptable;
- If the temperature measuring device is used over a range of greater than 10°C, then the verification must bracket the range of use.

IR thermometers, digital probes and thermocouples are calibrated quarterly. IR Thermometers should be calibrated over the full range of use, including ambient, iced (4 ºC) and frozen (0 ºC to -5 ºC) per the Drinking Water Manual.

The mercury NIST thermometer is recalibrated every five years (unless thermometer has been exposed to temperature extremes or apparent separation of internal liquid) by an approved outside service and the provided certificate of traceability is kept on file. The NIST thermometer(s) have increments of 0.2 ºC, and has a range applicable to all method and certification requirements. The NIST traceable thermometer is used for no other purpose than to calibrate other thermometers.

All of this information is documented in logbooks. Monitoring method-specific temperatures, including incubators, heating blocks, water baths, and ovens, is documented in method-specific logbooks or directly into the LIMS batch. More information on this subject can be found in the laboratory SOP UP-QA-034, *Thermometer Calibration* and the method-specific SOPs.

20.3.4 Refrigerators/Freezer Units, Waterbaths, Ovens and Incubators

The temperatures of all refrigerator units and freezers used for sample and standard storage are monitored continuously via an electronic monitoring system.

Ovens, water baths and incubators are monitored on days of use.

All of this equipment has a unique identification number, and is assigned a thermometer for monitoring.

Sample storage refrigerator temperatures are kept between > 0 °C and ≤ 6 °C. The electronic monitoring system applies the limits of 4 ± 2°C to comply with those projects that require the tighter monitoring window.

Specific temperature settings/ranges for other refrigerators, ovens, water baths, and incubators can be found in method specific SOPs.

The temperatures that are continuously monitored are stored electronically on the Local Area Network (LAN) and the method specific temperature documentation of ovens water baths and incubators are maintained within the individual method logbooks or LIMS batch records.

20.3.5 Autopipettors, Dilutors, and Syringes

Mechanical volumetric dispensing devices including burettes (except Class A Glassware) are given unique identification numbers and the delivery volumes are verified gravimetrically, at a minimum, on a quarterly basis. Glass micro-syringes are colored coded and disposed of quarterly and are considered the same as Class A glassware.

For those dispensers that are not used for analytical measurements, a label shall be applied to the device stating that it is not calibrated. Any device not regularly verified cannot be used for any quantitative measurements.

Micro-syringes are purchased from Hamilton Company. Each syringe is traceable to NIST. The laboratory keeps on file an “Accuracy and Precision Statement of Conformance” from Hamilton attesting established accuracy.

20.4 INSTRUMENT CALIBRATIONS

Calibration of analytical instrumentation is essential to the production of quality data. Strict calibration procedures are followed for each method. These procedures are designed to determine and document the method detection limits, the working range of the analytical instrumentation and any fluctuations that may occur from day to day.

Sufficient raw data records are retained to allow an outside party to reconstruct all facets of the initial calibration. Records contain, but are not limited to, the following: calibration date, method, instrument, analyst(s) initials or signatures, analysis date, analytes, concentration, response, type of calibration (Avg RF, curve, or other calculations that may be used to reduce instrument responses to concentration.)

Sample results must be quantitated from the initial calibration and may not be quantitated from any continuing instrument calibration verification unless otherwise required by regulation, method or program.

If the initial calibration results are outside of the acceptance criteria, corrective action is performed and any affected samples are reanalyzed if possible. If the reanalysis is not possible, any data associated with an unacceptable initial calibration will be reported with appropriate data qualifiers (refer to Section 14).

Note: Instruments are calibrated initially and as needed after that and at least annually.

20.4.1 CALIBRATION STANDARDS

Calibration standards are prepared using the procedures indicated in the Reagents and Standards section of the determinative method SOP. If a reference method does not specify the number of calibration standards, a minimum of 3 calibration points will be used.

20.4.1.1 For each analyte and surrogate (if applicable) of interest, prepare calibration standards at the minimum number of concentrations as stated in the analytical methods. If a reference method does not specify the number of calibration standards, a minimum of 3 calibration points (except being ICP and ICP/MS methods) will be used, not including blanks or a zero standard. All of the standard solutions are prepared using Class A volumetric glassware, calibrated pipettes, and/or micro-syringes and appropriate laboratory quality solvents and stock standards.

20.4.1.2 Standards for instrument calibration are obtained from a variety of sources. All standards are traceable to national or international standards of measurement or to national or international standard reference materials wherever possible. Dilution standards are prepared from stock standards purchased from commercial suppliers. The standards are entered into the reagent module of the LIMS system and are maintained for each department, containing concentration, date of receipt, date of standard preparation, any dilutions made, lot number, supplier, type of solvent and a unique code number to identify the standard.

20.4.1.3 The lowest concentration calibration standard that is analyzed during an initial calibration must be at or below the stated reporting limit for the method based on the final volume of extract (or sample). The exception to these rules is ICP and ICP/MS methods or other methods where the referenced method does not specify two or more standards.

20.4.1.4 The other concentrations define the working range of the instrument/method or correspond to the expected range of concentrations found in actual samples that are also within the working range of the instrument/method. Results of samples not bracketed by initial instrument calibration standards (within calibration range to at least the same number of significant figures used to report the data) must be reported as having less certainty, e.g., defined qualifiers or flags (additional information may be included in the case narrative). The lowest calibration standard must be at or below the reporting limit. The exception to these rules is ICP and ICPMS methods or other methods where the referenced method does not specify two or more standards.

20.4.1.5 All initial calibrations are verified with a standard obtained from a second source and traceable to a national standard, when available (or vendor certified different lot if a second source is not available). For unique situations where no other source or lot is available, a standard made by a different analyst would be considered a second source. This verification occurs immediately after the calibration curve has been analyzed, and before the analysis of any samples.

20.4.2 CALIBRATION FOR ORGANIC METHODS (GC, GC/MS)

20.4.2.1 Many of the organic analytical methods utilize an internal standard calibration. Because of the complex nature of the multi-peak chromatograms produced by the method, some instruments necessitate the use of external standard calibration (some GC methods). Surrogate compounds are included in the calibration processes for all appropriate organic analyses. For more details on the calibration types listed below, refer to the NDSC Document No. NDSC-QA-QP44940, Calibration Curves and the Selection of Calibration Points.

20.4.2.2 Once the operating parameters have been established according to the method, each instrument is calibrated for the appropriate method. The analyst prepares five or more standard solutions at various concentrations containing all of the analytes of interest, internal standards, and surrogates that are appropriate for the method. Note: There are several EPA methods that have different requirements and are exceptions where a minimum of 3 calibration standards are prepared and analyzed.

20.4.2.3 The standard solutions are introduced into the instrument in the same manner as samples: by direct injection, by headspace analysis, or by purge and trap. The calibration factor (CF) for methods that use external standards, and the response factor (RF) for methods that use internal standards are calculated for the five standards.

- External standard calibration involves comparison of instrument responses from the sample to the responses from the target compounds in the calibration standards. Sample peak areas (or peak heights) are compared to peak areas (or heights) of the standards. The ratio of the response to the amount of analyte in the calibration standard is defined as the Calibration factor (CF).

- Internal standard calibration involves the comparison of instrument responses from the target compounds in the sample to the responses of specific standards added to the sample or sample extract prior to injection. The ratio of the peak area (or height) of the target compound in the sample or sample extract to the peak area (or height) of the internal standard in the sample or sample extract is compared to a similar ratio derived for each calibration standard. The ratio is termed the response factor (RF), and may also be known as a relative response factor in other methods.

In many cases, internal standards are recommended. These recommended internal standards are often brominated, fluorinated, or stable isotopically labeled analogs of specific target compounds, or are closely related compounds whose presence in environmental samples is highly unlikely. The use of specific internal standards is available in the method SOP.

Whichever internal standards are employed, the analyst needs to demonstrate that the measurement of the internal standard is not affected by method analytes and surrogates or by matrix interferences. The use of MS detectors makes internal standard calibration practical because the masses of the internal standards can be resolved from those of the target compounds even when chromatographic resolution cannot be achieved.

When preparing calibration standards for use with internal standard calibration, add the same amount of the internal standard solution to each calibration standard, such that the concentration of each internal standard is constant across all of the calibration standards, whereas the concentrations of the target analytes will vary. The internal standard solution will contain one or more internal standards and the concentration of the individual internal standards may differ within the spiking solution (e.g., not all internal standards need to be at the same concentration in this solution). The mass of each internal standard added to each sample extract immediately prior to injection into the instrument or to each sample prior to purging must be the same as the mass of the internal standard in each calibration standard. The volume of the solution spiked into sample extracts should be such that minimal dilution of the extract occurs (e.g., 10 uL of solution added to a 1 mL final extract results in only a negligible 1% change in the final extract volume which can be ignored in the calculations).

An ideal internal standard concentration would yield a response factor of 1 for each analyte. However, this is not practical when dealing with more than a few target analytes. Therefore, as a general rule, the amount of internal standard should produce an instrument response (e.g., area counts) that is no more than 100 times that produced by the lowest concentration of the least responsive target analyte associated with the internal standard. This should result in a minimum response factor of approximately 0.01 for the least responsive target compound. Refer to the NDSC Document No. NDSC-QA-QP44940, Calibration Curves and the Selection of Calibration Points, for specific calculations.

20.4.2.4 Policies regarding the use of calibration standard results for creating the calibration curve are as follows:

- A low calibration standard may be excluded from the calibration if the signal-to-noise ratio or spectral criteria are not suitable. The reporting level must be elevated to be the lowest calibration standard used for calibration.
- The upper calibration standard may be excluded if it saturates the detector or is obviously becoming non-linear. Any sample exceeding the upper standard used in the calibration must be diluted and re-analyzed.
- Mid-calibration standards may not be excluded unless an obvious reason is found, i.e., cracked vial, incorrectly made, etc. The failed standard should be re-run immediately and inserted into the initial calibration. If not useful, recalibration is required.

20.4.2.5 Percent RSD Corrective Action

Given the potentially large numbers of analytes that may be analyzed in some methods, it is likely that some analytes may exceed the acceptance limit for the RSD for a given calibration. In those instances, the following steps are recommended, but not required.

20.4.2.5.1 The first step is generally to check the instrument operating conditions. This option will apply in those instances where a linear instrument response is expected. It may involve some trade-offs to optimize performance across all target analytes. For instance, changes to the operating conditions necessary to achieve linearity for problem compounds may cause the RSD for other compounds to increase, but as long as all analytes meet the RSD limits for linearity, the calibration is acceptable.

20.4.2.5.2 If the RSD for any analyte is greater than the applicable acceptance criteria in the applicable analytical method, analytical SOP or project specific QAPP, the analyst may wish to review the results (area counts, calibration or response factors, and RSD) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards. If the problem appears to be associated with a single standard, that one standard may be reanalyzed and the RSD recalculated. Replacing the standard may be necessary in some cases.

20.4.2.5.3 A third alternative is to narrow the calibration range by replacing one or more of the calibration standards with standards that cover a narrower range. If linearity can be achieved using a narrower calibration range, document the calibration linearity, and proceed with analyses. The changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end of the range.

Note: When the purpose of the analysis is to demonstrate compliance with a specific regulatory limit or action level, the laboratory must ensure that the method quantitation limit is at least as low as the regulatory limit or action level.

20.4.2.6 Alternatively, the least squares regression may be used to determine linearity for organic method calibrations. A five point line must result in a correlation coefficient (r) $\geq$ 0.995 or the coefficient of determination (r^2) must be $\geq$ 0.990 or better.

20.4.2.7 Instead of a linear curve model (either Average RF or least squares regression), a second order curve (Quadratic) may be used (and preferred) as long as it contains at least six data points. As a rule of thumb, if there is a consistent trend in RFs (or CFs) in the calibration curve, either up or down, then quadratic curve fit may be indicated as the preferred calibration routine for that analyte. The coefficient of determination (COD or r^2) for the quadratic curve must be at least 0.99 for it to be considered acceptable. For more details on the calculations see the NDSC Document No. NDSC-QA-QP44940, Calibration Curves and the Selection of Calibration Points. There are some limitations on the use of Quadratic Curve fits:

20.4.2.7.1 Care MUST be exercised to assure that the results from this equation are real, positive, and fit the range of the initial calibration.

20.4.2.7.2 They **may not** be used to mask instrument problems that can be corrected by maintenance. (Not to be used where the analyte is normally found to be linear in a properly maintained instrument).

20.4.2.7.3 They **may not** be used to compensate for detector saturation. If it is suspected that the detector is being saturated at the high end of the curve, remove the higher concentration standards from the curve and try a 1st order fit or average RF.

20.4.3 Calibration for Inorganic Analyses

EPA Method 7000 from EPA SW-846 is a general introduction to the quality control requirements for metals analysis. For inorganic methods, quality control measures set out in the individual methods and in the *Standard Methods for the Examination of Water and Wastewater* (20th Edition) may also be included. Standard Operating Procedures for the analysis and the quality control documentation measures are kept in the individual laboratory areas.

In general, inorganic instrumentation is calibrated with external standards. Some exceptions would be Inductively Coupled Plasma (ICP) and Inductively Coupled Plasma Mass Spec (ICPMS). These analyses may use an internal standard to compensate for viscosity or other matrix effects. While the calibration procedures are much the same for inorganics as they are for organics, CF's or RF's are not used. The calibration model in 20.4.2.6 is generally used for most methods, however in some instances the model from section 20.4.2.7 may be used. A correlation coefficient (r) of 0.995 or greater must be used to accept a calibration curve generated for an inorganic procedure. Correlation coefficients are determined by computer programs and documented as part of the calibration raw data. Coefficients of calibration curves used for quantitation must be documented as part of the raw data. Curves are not allowed to be stored in calculator memories and must be written on the raw data for the purposes of data validation.

20.4.3.1 "Calibrations" for titrimetric analyses are performed by standardizing the titrants against a primary standard solution. See specific methods in *Standard Methods for the Examination of Water and Wastewater* (20th Edition) for more information.

20.4.3.2 Spreadsheets that are used for general chemistry calculations must have all cells containing calculations locked to prevent accidental changes to the calculations.

20.4.4 Calibration Verification

The calibration relationship established during the initial calibration must be verified at least daily as specified in the laboratory method SOPs in accordance with the referenced analytical methods and in the 2009 and 2016 TNI Standard. The process of calibration verification applies to both external standard and internal standard calibration techniques, as well as to linear and non-linear calibration models. Initial calibration verification (ICV) is with a standard source secondary (second source standard) to the calibration standards, but continuing calibration verifications (CCV) may use the same source standards as the calibration curve.

Note: The process of calibration verification referred to here is fundamentally different from the approach called "calibration" in some methods. As described in those methods, the calibration factors or response factors calculated during calibration are used to update the calibration factors or response factors used for sample quantitation. This approach, while employed in other EPA programs, amounts to a daily single-point calibration.

All target analytes and surrogates, including those reported as non-detects, must be included in periodic calibration verifications for purposes of retention time confirmation and to demonstrate that calibration verification criteria are being met, i.e., RPD, per 2009 and 2016 TNI Standard, EL-V1M4 Sec. 1.7.2.

All samples must be bracketed by periodic analyses of standards that meet the QC acceptance criteria (e.g., calibration and retention time). The frequency is found in the determinative methods or SOPs or project specific QAPPs.

Note: If an internal standard calibration is being used (basically GCMS) then bracketing standards are not required, only daily verifications are needed. The results from these verification standards must meet the calibration verification criteria and the retention time criteria (if applicable).

20.4.4.1 Generally, the calibrations must be verified at the beginning of each 12-hour analytical shift during which samples are analyzed. The ICV may be used as the first bracketing CCV, if criteria for both are met.

20.4.4.2 A continuing instrument calibration verification (CCV) is generally analyzed at the beginning of each 12-hour analytical shift during which samples are analyzed. The 12-hour analytical shift begins with the injection of the calibration verification standard (or the MS tuning standard in MS methods). The shift ends after the completion of the analysis of the last sample, QC, or standard that can be injected within 12-hours of the beginning of the shift. For methods that have quantitation by external calibration models, a CCV is analyzed at the end of each analytical sequence. Some methods have more frequent CCV requirements. See specific SOPs. Most Inorganic methods require the CCV to be analyzed after ever 10 samples or injections, including matrix or batch QC samples.

20.4.4.3 The acceptance limits for calibration verifications can be found in each method SOP. As a rule of thumb: GCMS ± 20% (for CCC's), GC ± 15% or ± 20%, Inorganics: ± 10 or ± 15%. Actual methods may have wider or tighter limits; see the method SOP for specifics, also refer to Appendix 4.

20.4.4.4 If the response (or calculated concentration) for an analyte is within the acceptance limits of the response obtained during the initial calibration, then the initial calibration is considered still valid, and the analyst may continue to use the CF, RF or % drift values from the initial calibration to quantitate sample results.

20.4.4.5 If calibration verification, ICV or CCV, acceptance criteria are not met, then the problem should be investigated and corrected prior to sample analysis. Corrective actions vary by instrument and method (as described in method SOPs), but typically include:

- Checking instrument settings and SOPs to ensure there is no operator error,
- Rerunning the calibration verification standard,
- Repreparing and reanalyzing the verification standard,
- Performing routine instrument maintenance*,
- If the CCV still fails, then the instrument should be recalibrated and associated samples reanalyzed.

*If routine maintenance such as injection port cleaning, contaminated column clipping, guard column replacement, etc. are needed to pass the CCV, the associated field samples shall be reanalyzed. The only corrective action for passing CCV without the need of reanalysis of previous samples is preparing and using fresh CCV standards.

If the results of a CCV are outside the established acceptance criteria and analysis of a second consecutive (and immediate) CCV fails to produce results within acceptance criteria, corrective

action shall be performed. Once corrective actions have been completed & documented, the laboratory shall demonstrate acceptable instrument / method performance by analyzing two consecutive CCVs, or a new initial instrument calibration shall be performed.

Sample analyses and reporting of data may not occur or continue until the analytical system is calibrated or calibration verified. However, data associated with an unacceptable calibration verification check may be fully useable under the following special conditions:

a). when the acceptance criteria for the CCV are exceeded high (i.e., high bias) and the associated samples within the batch are non-detects, then those non-detects may be reported with a case narrative comment explaining the high bias. Otherwise the samples affected by the unacceptable CCV shall be re-analyzed after a new calibration curve has been established, evaluated and accepted; or

b). when the acceptance criteria for the CCV are exceeded low (i.e., low bias), those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable CCV shall be re-analyzed after a new calibration curve has been established, evaluated and accepted.

All target analytes and surrogates, including those reported as non-detects, must be included in periodic calibration verifications for purposes of retention time confirmation and to demonstrate that calibration verification criteria are being met.

Where required by method or project QAPP, all samples must be bracketed by periodic analyses of standards that meet the QC acceptance criteria (e.g., calibration and retention time). The frequency is found in the determinative methods or SOPs.

Note: If an internal standard calibration is being used (e.g. GC/MS), then bracketing standards are not required, only daily verifications are needed, except as specified by program or method requirements.

20.4.4.6 Verification of Linear and Non-Linear Calibrations

Calibration verification for linear calibrations involves the calculation of the percent drift or the percent difference of the instrument response between the initial calibration and each subsequent analysis of the verification standard. (These calculations are available in the laboratory method SOPs.) Verification standards are evaluated based on the % Difference from the average CF or RF of the initial calibration or based on % Drift or % Recovery if a linear or quadratic curve is used.

Regardless of whether a linear or non-linear calibration model is used, if initial verification criterion is not met, then no sample analyses may take place until the calibration has been verified or a new initial calibration is performed that meets the specifications listed in the method SOPs. If the calibration cannot be verified after the analysis of a single verification standard, then adjust the instrument operating conditions and/or perform instrument maintenance, and analyze another aliquot of the verification standard. If the calibration cannot be verified with the second standard, then a new initial calibration is performed.

- When the acceptance criteria for the calibration verification are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise, the samples affected by the unacceptable calibration verification shall be reanalyzed after a new calibration curve has been established, evaluated and accepted.
- When the acceptance criteria for the calibration verification are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise, the samples affected by the unacceptable verification shall be reanalyzed after a new calibration curve has been established, evaluated and accepted. Alternatively, a reporting limit standard may be analyzed to demonstrate that the laboratory can still support non-detects at their reporting limit.

20.5 TENTATIVELY IDENTIFIED COMPOUNDS (TICS) – GC/MS ANALYSIS

For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

Note: If the TIC compound is not part of the client target analyte list but is calibrated by the laboratory and is both qualitatively and/or quantitatively identifiable, it should not be reported as a TIC. If the compound is reported on the same form as true TICs, it should be qualified and/or narrated that the reported compound is qualitatively and quantitatively (if verification in control) reported compared to a known standard that is in control (where applicable).

20.5.1 Use the following guidelines for making tentative identifications

20.5.1.1 Major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

20.5.1.2 The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

20.5.1.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

20.5.1.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co eluting compounds.

20.5.1.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

The concentration of any non-target analytes identified in the sample (see above) should be estimated. The same formula as calibrated analytes should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

Note: The above guidelines above are from EPA SW846 III edition, method 8260B.
For general reporting if TICs are requested, the ten (10), largest non-target analyte peaks whose area count exceeds 10% of the nearest internal standard will be termed “Tentatively Identified Compounds” (TICs). More or fewer TICs may be identified based on client requirements.

20.5.2 TIC Reporting Limits

In general reporting limits cannot be specified because of the unknown nature of the TIC. Any reporting limit that is assigned to the TIC can only be evaluated as an estimate as the quantitation is based on the assumption that the TIC responds exactly as the IS responds which is most likely not the case. The TALs data report does not report TICs with a referenced

reporting limit. Note: The reporting of Targeted TICs by methods 8270D/E, 625 and 625.1 have an associated reporting limit at a concentration that has been verified as being detected and discernable from a blank.

TICs that meet the above identification criteria (Section 20.5.1) at 10% area of the IS: If a RL were to be assigned, it would be 10% of the concentration of the internal standard used for quantitation. (e.g. 2.5 ug/L for 8260B, 4.0 ug/L for 8270D/E). In general, if the 10% area criteria are not met, the TIC RLs should be set at a level approximately 5x the level of the poorest performer in the analysis.

20.6 GC/MS TUNING

Prior to any GCMS analytical sequence, including calibration, the instrument parameters for the tune and subsequent sample analyses within that sequence must be set.

Prior to tuning/auto-tuning the mass spectrometer, the parameters may be adjusted within the specifications set by the manufacturer or the analytical method. These generally don't need any adjustment but it may be required based on the current instrument performance. If the tune verification does not pass it may be necessary to clean the source or perform additional maintenance. Any maintenance is documented in the maintenance log.

20.6.1 The concentration of the BFB or DFTPP must be at or below the concentrations that are referenced in the analytical methods. Part of the purpose of the tune is to demonstrate sensitivity and analyzing solutions at higher concentrations does not support this purpose. Tune failures may be due to saturation and a lower BFB/DFTPP concentration may be warranted.

20.6.2 Tune evaluations usually utilize the "Autofind" function and are set up to look at the apex +/- 1 scan and average the three scans. Background correction is required prior to the start of the peak but no more than 20 scans before. Background correction cannot include any part of the target peak.

20.6.3 Other Options or if Auto Tune Fails:

20.6.3.1 Sometimes the instrument does not always correctly identify the apex on some peaks when the peak is not perfectly shaped. In this case, manually identify and average the apex peak +/- 1 scan and background correct as in 20.6.2 above. This is consistent with EPA 8260B and 8270D/E.

20.6.3.2 Or the scan across the peak at one half peak height may be averaged and background corrected. This is consistent with Standard Methods 6200, EPA 624/624.1 and EPA 625/625.1.

20.6.3.3 Adjustments such as adjustments to the repeller and ion focus lenses, adjusting the EM Voltage, etc. may be made prior to tune verification as long as all of the subsequent injections in the 12 hour tune cycle are analyzed under the same MS tune settings and it is documented in the run sequence log and/or maintenance log that an adjustment was made. Excessive adjusting (more than 2 tries) without clear documentation is not allowed. Necessary maintenance is performed and documented in instrument log.

20.6.3.4 A single scan at the Apex (only) may also be used for the evaluation of the tune or as specified in the reference method. For SW 846 and EPA 600 series methods, background correction is still required.

20.6.3.5 Cleaning the source or other maintenance may be performed and then follow steps for tune evaluation above. Note: If significant maintenance was performed, see methods 8000B or 8000C then the instrument may require recalibration prior to proceeding.

20.6.4 Tune evaluation printouts must include the chromatogram and spectra as well as the Tune evaluation information. In addition, the verifications must be sent directly to the printer or pdf file (no screen prints for DFTPP or BFB tunes). This ability should be built into the instrument software.

20.6.5 All MS tune settings must remain constant between running the tune check and all other samples. It is recommended that a separate tune method not be used, however a separate method may be used as long as the MS conditions between the methods are the same as the sample analysis method and tracked so any changes that are made to the analysis method are also made to the tune method.

Table 20-1.

Example - Laboratory Equipment and Instrumentation

Equipment/ Instrument	Manufacturer	Model Number	Serial Number	Year Put into Service	Condition When Received
GC Extractable INST1920_DRO	Agilent 7890A GC System with dual FID	7890A (G3440A)	S/N CN10501115	2011	NEW
GC Extractable INST2324_PCB	Agilent 6890N GC System with Dual ECD	G6890N (G1530N)	S/N CN10421024	2004	NEW
GC Extractable INST2526_DRO	Agilent 7890A GC System with dual FID	7890A (G3440A)	S/N CN10371134	2010	NEW
GC Extractable INST2930_WIDRO	Agilent 7890A GC System with dual FID	7890A (G3440A)	S/N CN10848171	2011	NEW
GC Extractable INST3132_PCB	Agilent 6890N GC System with dual ECD	6890N (G1530N)	S/N CN10411047	2004	NEW
GC Extractable INST3738_PEST	HP 6890 Series GC with Dual ECD	6890 (G1530A)	S/N US00004455	1996	NEW
GC Extractable INST5354_PEST	Agilent 8860 Series GC with Dual ECD	8860 (G2790A)	S/N CN2108D002	2021	NEW
GC Extractable INST4950_HERB	HP 6890 Series GC with Dual ECD	6890 (G1530A)	S/N US00006442	2015	USED
GC Extractable INST5556_HERB	Agilent 8860 Series GC with Dual ECD	8860 (G2790A)	S/N CN2117D007	2021	NEW
GC Extractable INST4748_PCB	Agilent 6890A Series GC Plus with Dual ECD	6890A (G1530A)	S/N US00037876	2007	NEW
GC Extractable INST5152_PCB	Agilent 6890A Series GC with Dual ECD	6890A (G1530A)	S/N US00039258	2019	USED
GC Volatile INST1314_GRO	Agilent 7890 GC with FID	7890	S/N CN10291030	2010	NEW
GC Volatile INST57_GRO	Agilent 8860 Series GC with FID	8860	S/N CN2112D001	2021	NEW

Equipment/ Instrument	Manufacturer	Model Number	Serial Number	Year Put into Service	Condition When Received
GC/MS Semivolatile CMS01	Agilent 6890N GC System Agilent 5973 MS Detector	6890N (G1530N) G2578A	S/N US10250131 S/N US21854134	2004	NEW
GC/MS Semivolatile CMS11	Agilent 6890N GC System Agilent 5973 MS Detector	6890N (G1530N) G2578A	S/N CN10308018 S/N US30955129	2003	NEW
GC/MS Semivolatile CMS12	Agilent 6890N GC System Agilent 5973 MS Detector	6890N (G1530N) G2578A	S/N CN10308019 S/N US21854871	2003	NEW
GC/MS Semivolatile CMS20	Agilent 6890N GC System Agilent 5975 MS Detector	6890N (G1530N) G3171A	S/N CN10615045 S/N US861622903	2006	NEW
GC/MS Semivolatile CMS21	Agilent 6890A GC System Agilent 5973 MS Detector	6890A (G1530A) G2577A	S/N US00035156 S/N US10442182	2008	USED
GC/MS Semivolatile CMS23	Agilent 7890A GC System Agilent 5975C MS Detector	7890A (G3440A) 5975C (G3172A)	S/N CN10271149 S/N US10283612	2010	NEW
GC/MS Semivolatile CMS24	Agilent 7890A GC System Agilent 5975C MS Detector	7890A (G3440A) 5975C (G3172A)	S/N CN10211009 S/N US10323620	2011	NEW
GC/MS Semivolatile CMS30	Agilent 6890 GC System Agilent 5973 MS Detector	6890A (G1530A) 5973 (G1099A)	S/N US00021127 S/N US80321385	2019	USED
GC/MS Volatile CMS02	Agilent 6890N GC System Agilent 5973 MS Detector	6890N (G1530N) G2579A	S/N CN10340024 S/N US33220076	2003	NEW
GC/MS Volatile MS03 (Screener)	HP 5890 Series II GC HP 5972 Series MS Detector	5890 Series II 5972	S/N 3310A47330 S/N 3609A03585	1998	NEW
GC/MS Volatile CMS06	Agilent 6890 Series GC Plus G1530A Agilent 5973 Network MS Detector G2579A	6890 (G1530A) 5973 (G2579A)	S/N US10250132 S/N US21854172	2003	NEW
GC/MS Volatile CMS16	Agilent 6890 Series GC Plus G1530A Agilent 5973 Network MS Detector G2579A	6890 (G1530A) 5973 (G2579A)	S/N US00041196 S/N US10360253	2001	NEW
GC/MS Volatile CMS18	Agilent 6890N Series GC Agilent 5975 Series MS Detector	6890N Series (G1530N) 5975 (G3172A)	S/N CN10528010 S/N US51530111	2005	NEW
GC/MS Volatile CMS19	Agilent 6890N Series GC Agilent 5975 Series MS Detector	6890N Series (G1530N) 5975 (G3172A)	S/N CN10527059 S/N US52430414	2005	NEW

Equipment/ Instrument	Manufacturer	Model Number	Serial Number	Year Put into Service	Condition When Received
GC/MS Volatile CMS22	Agilent 6890N Series GC Agilent 5973 Series MS Detector	6890N Series (G1530N) 5973 (G2571A)	S/N US10202110 S/N US10442062	2008	USED
GC/MS Volatile CMS25	Agilent 7890A Series GC Agilent 5975C Series MS Detector	7890A Series (G3440A) 5975 (G3712A)	S/N CN10934049 S/N US92033656	2009	USED
GC/MS Volatile CMS27 (Screener)	Agilent 6890 Series GC Agilent 5973 Series MS Detector	6890 Series (G1530A) 5973 (G1099A)	S/N DE00020179 S/N US81221508	2013	USED
GC/MS Volatile CMS28 (Screener)	Agilent 6890 Series GC Agilent 5973 Series MS Detector	6890 Series (G1530A) 5973 (G1098A)	S/N US00024781 S/N US82311399	2013	USED
GC/MS Volatile CMS29	Agilent 7890B Series GC Agilent 5977B Series MS Detector	7890 Series (G3440B) 5977 (G7077B)	S/N CN18023170 S/N US1813M041	2018	NEW
Autoanalyzer SEAL2	SEAL AQ2 Analyzer	AQ2	S/N 090867	2013	NEW
Autoanalyzer SEAL3	SEAL AQ2 Analyzer	AQ700	S/N 070019	2023	NEW
Autoanalyzer PC Titrate	Burivar - I/2 Buret Module	PC-1104-00	S/N MS-0E3-585	2004	NEW
Discrete Analyzer Galley 1	Thermo Fisher Scientific Gallery Plus Autoanalyzer	Gallery Plus	862000113075	2020	NEW
Discrete Analyzer SYSTEA	Systea Discrete Analyzer	EasyChem Plus	S/N 0900268	2011	NEW
Discrete Analyzed SYSTEA3	Systea Discrete Analyzer	EasyChem Plus	S/N 2006E 1001205	2019	USED
Ion Chromatography IC6C	Dionex ICS-1100 Ion Chromatograph	ICS-1100	S/N 13040962	2013	NEW
Ion Chromatography IC7C	Dionex ICS-5000 Ion Chromatograph	ICS-SP-5	S/N 11120709	2014	USED
Ion Chromatography IC8C	Dionex ICS-1100 Ion Chromatograph	ICS-1100	S/N 14082507	2014	NEW
Ion Chromatography IC9	Dionex Integrion RFIC	Integrion	S/N 23083164	2024	NEW
TOC TOC5	Teledyne-Tekmar TOC Analyzer	FUSION	S/N US10216006	2010	NEW
TOC TOC6	TOC – Shimadzu	TOC L	S/N H54315632068	2018	NEW
Dissolved Oxygen Meter HACH-DO1	Sension6 Dissolved Oxygen Meter	Sension6	S/N 990400000150	1999	NEW
Dissolved Oxygen Meter HACH-DO2	Sension6 Portable Dissolved Oxygen Meter	Sension6	S/N 040400002840	2002	NEW

Equipment/ Instrument	Manufacturer	Model Number	Serial Number	Year Put into Service	Condition When Received
Dissolved Oxygen Meter HACH-DO3	HACH HQ40d Portable Dissolved Oxygen Meter	HG40d	None	2012	USED
PC BOD BOD2	Mantech Automax 372 PC BOD	PC-1000-1073	MT-1G9-111	2019	NEW
Flashpoint Tester FP6	Flashpoint Tester – Koehler – Closed Cup	K71000	S/N K7100010155C	2022	NEW
Flashpoint Tester FP5	Flashpoint Tester – Koehler - Open Cup	K13902	S/N K1390210037B	2017	NEW
pH Meter 2874	pH Meter: Thermo Orion	STAR A211	S/N X19593	2014	NEW
pH Meter 2855	pH Meter: Thermo Orion	STAR A211	S/N X18061	2014	NEW
pH Meter 2939	pH Meter: Thermo Orion	Orion 3 STAR	S/N 23350	2013	NEW
pH Meter 3101	pH Meter: Thermo Orion	STAR A211	S/N X33328	2016	NEW
pH Meter 3195	pH Meter: Thermo Orion	STAR A211	S/N X48056	2019	NEW
pH Meter 3366	pH Meter: Thermo Orion	STAR A211	S/N X51328	2021	NEW
pH Meter 3367	pH Meter: Thermo Orion	STAR A211	S/N X58344	2021	NEW
pH_Auto1	Mantech Automax 122 Sampler	PC-1000-688	S/N 261A3N031	2019	USED
Oil & Grease	Horizon Technology: Oil & Grease Machine – Extractor	SPE-3000XL Plus-SS	S/N 04-2008	2005	NEW
Oil & Grease	Horizon Technology: Oil & Grease Controller	SPE-DEX 1000/3000XL	S/N 09-1131	2009	NEW
Oil & Grease	Speed Vap II – Evaporator	SPEED-VAP 9000	S/N 02-0389	2002	NEW
Oil & Grease	Horizon Technology: Oil & Grease Controller	SPE-DEX 3000XL	S/N 10-1255	2011	NEW
Oil & Grease	Horizon Technology: Oil & Grease Machine – Extractor	SPE-DEX 1000 / 3000XL	S/N 10-1866	2011	NEW
Oil & Grease	Speed Vap III – Evaporator	SPEED-VAP III	S/N 13-0862	2013	NEW
rAPIDT-1	Astoria Pacific: rAPID-T Autoanalyzer 4600	4600	S/N 4660-1064	2019	NEW
rAPIDT-2	Astoria Pacific: rAPID-T Autoanalyzer 4600	4600	S/N 4660-1075	2019	NEW
rAPIDT-3	Astoria Pacific: rAPID-T Autoanalyzer 4600	4600	S/N 4660-1069	2019	NEW
rAPIDT-4	Astoria Pacific: rAPID-T Autoanalyzer 4600	4600	S/N 4660-1073	2019	NEW
Conductivity Meter	Specific Conductivity Meter: VWR EC Meter	1056	S/N 0104022	2001	NEW
Turbidimeter TURB2	Turbidimeter : VWR Scientific	66120-200	S/N TUB800-2393	2011	NEW
Mercury CV Analyzer HG6	Teledyne Leeman Hydra II Auto Mercury Analyzer	HYDRA II	S/N 0023	2010	NEW
Mercury CV Analyzer HG7	Quick Trace – M-7600 Mercury Analyzer	M-7600	S/N US18193015	2018	NEW
ICP ICP6	Thermo Fisher ICAP 6500 DUO	6500 DUO	S/N 20083806	2008	NEW
ICP ICP8	Thermo ICAP 6000 DUO	6000 DUO	S/N 20102205	2013	USED
ICP ICP10	Thermo ICAP 6500 DUO	6500 DUO	S/N 20110815	2022	USED

Equipment/ Instrument	Manufacturer	Model Number	Serial Number	Year Put into Service	Condition When Received
ICP-MS ICPMS4	Agilent ICP-MS 7700X-Series Agilent Autosampler ASX-500	7700X-Series (G3281A) ASX-500	S/N JP11040848 S/N S020798A520	2013	USED
ICP-MS ICPMS6	Agilent 7850 Series Agilent Autosample SPS4	7850 Series SPS4	S/N Sg23311436 S/N AU232516287	2018	USED
TCLP-48 Extraction Apparatus	TCLP Rotation System: Associated Designer & Manufacturer	3740-48BRE	S/N 2244	2010	NEW
TCLP-48 Extraction Apparatus	TCLP Rotation System: Associated Designer & Manufacturer	3740-48BRE	S/N 07142378	2014	NEW
TCLP-12 Extraction Apparatus	TCLP Rotation System: Environmental Express LE Rotator	GF18N060-BMYJ1C	8212 12 631	2012	NEW
TCLP-12 Extraction Apparatus	TCLP Rotation System: Environmental Express LE Rotator	GF18N060-BMYJ1C	8212 12 632	2012	NEW

SECTION 21

MEASUREMENT TRACEABILITY

21.1 OVERVIEW

Traceability of measurements shall be assured using a system of documentation, calibration, and analysis of reference standards. Laboratory equipment that are peripheral to analysis and whose calibration is not necessarily documented in a test method analysis or by analysis of a reference standard shall be subject to ongoing certifications of accuracy. At a minimum, these must include procedures for checking specifications of ancillary equipment: balances, thermometers, temperature, Deionized (DI) and Reverse Osmosis (RO) water systems, automatic pipettes and other volumetric measuring devices. (Refer to Section 20.3) With the exception of Class A Glassware, quarterly accuracy checks are performed for all mechanical volumetric devices. Microsyringes (which come with a certificate of accuracy) are verified quarterly or disposed of after 3 months of use. Wherever possible, subsidiary or peripheral equipment is checked against standard equipment or standards that are traceable to national or international standards. Class A Glassware should be routinely inspected for chips, acid etching or deformity. If the Class A glassware is suspect, the accuracy of the glassware will be assessed prior to use.

The following definitions are provided by the American Association for Laboratory Accreditation (A2LA):

"Traceability is the property of a measurement result whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons, each step in the chain having stated uncertainties." There are six essential elements:

- An unbroken chain of comparison
- A calculated measurement uncertainty for each step in the chain to allow for an overall uncertainty calculation

- Documentation of each step in each calibration report
- All steps in the chain are performed by individuals with evidence of technical competence and accredited by a recognized accreditation body
- Reference to International Standard (SI) units
- Recalibration at appropriate intervals to preserve traceability

Calibration is defined as "determining and documenting the deviation of the indication of a measuring instrument (or the stated value of a material measure) from the conventional 'true' value of the measurand."

Uncertainty is defined as "a parameter associated with the result of a measurement that characterizes the dispersion of the value that could reasonably be attributed to the measurand." Measurement of Uncertainty is discussed is Section 19.12 of this QA Manual.

Note: Total measurement error is a function of both precision and bias.

21.2 NIST-TRACEABLE WEIGHTS AND THERMOMETERS

Reference standards of measurement shall be used for calibration only and for no other purpose, unless it can be shown that their performance as reference standards would not be invalidated.

For NIST-traceable weights and thermometers, the laboratory requires that all calibrations be conducted by a calibration laboratory accredited by A2LA, NVLAP (National Voluntary Laboratory Accreditation Program), or another accreditation organization that is a signatory to a MRA (Mutual Recognition Arrangement) of one or more of the following cooperations – ILAC (International Laboratory Accreditation Cooperation) or APLAC (Asia-Pacific Laboratory Accreditation Cooperation). A calibration certificate and scope of accreditation is kept on file at the laboratory. (Refer to Section 20.3 for calibration of weights and thermometers).

An external certified service engineer services laboratory balances on an annual basis. This service is documented on each balance with a signed and dated certification sticker. Balance calibrations are checked each day of use. All in-service thermometers are calibrated annually against a traceable reference thermometer. Temperature readings of ovens, refrigerators, and incubators are checked on each day of use or continuously monitored.

21.3 REFERENCE STANDARDS / MATERIALS

Commercially prepared reference standards, to the extent available, are purchased from vendors that are accredited to ISO Guide 34 and ISO/IEC Guide 17025. All reference standards from commercial vendors shall be accompanied with a certificate that includes at least the following information:

- Manufacturer
- Analytes or parameters calibrated
- Identification or lot number
- Calibration method
- Concentration with associated uncertainties
- Purity

If a standard cannot be purchased from a vendor that supplies a Certificate of Analysis, the purity of the standard is documented by analysis. (Refer to Section 11 for additional information on purchasing). The receipt of all reference standards must be documented. Reference standards are labeled with a unique Standard Name in LIMs and expiration date. All documentation received with the reference standard is retained as a QC record and references the LIMS assigned Standard Name.

All reference, primary and working standards/materials, whether commercially purchased or laboratory prepared, must be checked regularly to ensure that the variability of the standard or material from the true value does not exceed method requirements. The accuracy of calibration standards is checked by comparison with a standard from a second source. In cases where a second standard manufacturer is not available, a vendor certified different lot is acceptable for use as a second source. For unique situations, where no other source or lot is available, a standard made by a different analyst would be considered a second source. The appropriate Quality Control (QC) criteria for specific standards are defined in laboratory SOPs. In most cases, the analysis of an Initial Calibration Verification (ICV) or LCS (where there is no sample preparation) is used as the second source confirmation. These checks are generally performed as an integral part of the analysis method (e.g. calibration checks, laboratory control samples).

All standards and materials must be stored and handled according to method or manufacturer's requirements in order to prevent contamination or deterioration. Refer to Table 11-1 in Section 11 for general storage requirements, the Environmental Health & Safety Manual or individual laboratory SOPs. For safety requirements, please refer to method SOPs and the laboratory Environmental Health and Safety Manual.

Standards and reference materials shall not be used after their expiration dates unless their reliability is verified by the laboratory and their use is approved by the Quality Assurance Manager. The laboratory must have documented contingency procedures for re-verifying expired standards.

21.4 DOCUMENTATION AND LABELING OF STANDARDS, REAGENTS, AND REFERENCE MATERIALS

Reagents must be at a minimum the purity required in the test method. The date of reagent receipt and the expiration date are documented. The lots for most of the common solvents and acids are tested for acceptability prior to company-wide purchase. (Refer to NDSC Document No. NDSC-QA-SOP46704, Acid & Solvent Testing and Approval Program.)

All manufacturer or vendor supplied Certificate of Analysis or Purity must be retained, stored appropriately, and readily available for use and inspection. These records are maintained in the various laboratory sections. Records must be kept of the date of receipt and date of expiration of standards, reagents and reference materials. In addition, records of preparation of laboratory standards, reagents, and reference materials must be retained, stored appropriately, and be readily available for use and inspection. For detailed information on documentation and labeling, please refer to the method specific SOPs.

Commercial materials purchased for preparation of calibration solutions, spike solutions, etc.., are usually accompanied with an assay certificate or the purity is noted on the label. If the assay purity is 96% or better, the weight provided by the vendor may be used without correction. If the assay purity is less than 96% a correction will be made to concentrations applied to solutions prepared from the stock commercial material. Blended gas standard cylinders use a nominal concentration if the certified value is within +/- 15%, otherwise the certified value is used for the canister concentration.

21.4.1 All standards, reagents, and reference materials must be labeled in an unambiguous manner. Standards are logged into the laboratory's LIMS system in the reagent module, and are assigned a unique identification number. The following information is typically recorded in the electronic database within the LIMS.

• Standard Name	• Standard source type (stock or daughter)

• Description of Standard	• Standard type (spike, surrogate, other)
• Department	• Parent standard ID (if applicable)
• Preparer's name	• Parent Standard Analyte Concentration (if applicable)
• Final volume and number of vials prepared	• Parent Standard Amount used (if applicable)
• Solvent type and lot number	• Component Analytes
• Preparation Date	• Final Concentration of each analyte
• Expiration Date	

Records are maintained electronically for standard and reference material preparation. These records show the traceability to purchased stocks or neat compounds. These records also include the method of preparation, date of preparation, expiration date and preparer's name or initials. Preparation procedures are provided in the Method SOPs.

21.4.2 All standards, reagents, and reference materials must be clearly labeled with a minimum of the following information:

- Expiration Date (include prep date for reagents)
- Standard ID – LIMS Name
- Special Health/Safety warnings if applicable

Records must also be maintained of the date of receipt for commercially purchased items or date of preparation for laboratory prepared items. Special Health/Safety warnings must also be available to the analyst. This information is maintained in the analytical SOPs, the EH&S office in the form of SDS's and on the LAN.

21.4.3 In addition, the following information may be helpful:

- Date of receipt for commercially purchased items or date of preparation for laboratory prepared items
- Date opened (for multi-use containers, if applicable)
- Description of standard (if different from manufacturer's label or if standard was prepared in the laboratory)
- Recommended Storage Conditions
- Concentration (if applicable)
- Initials of analyst preparing standard or opening container

All containers of prepared reagents must include a preparation date, expiration date and an ID number to trace back to preparation.

Procedures for preparation of reagents can be found in the Method SOPs.

Standard ID numbers must be traceable through associated logbooks, worksheets and preparation/analytical batch records.

All reagents and standards must be stored in accordance to the following priority:
1) with the manufacturer's recommendations;
2) with requirements in the specific analytical methods; as specified in the laboratory SOP.

SECTION 22

SAMPLING

22.1 OVERVIEW

Eurofins Chicago provides sampling services. Sampling procedures for the bulleted items below are described in the laboratory SOP: UP-FS-001, *Field Services: Groundwater Sampling-Bailing Method*.

- Groundwater Sampling
- Wastewater Sampling
- Potable Sampling
- Field Parameter Analysis
- Cleaning and Decontamination of Field Equipment

22.2 SAMPLING CONTAINERS

The laboratory offers clean sampling containers for use by clients. These containers are obtained from reputable container manufacturers and meet EPA specifications as required. Certificates of cleanliness for bottles and preservatives are provided by the supplier are maintained at the laboratory. Alternatively, the certifications may be maintained by the supplier and available to the laboratory on-line.

22.2.1 Preservatives

Upon request, preservatives are provided to the client in pre-cleaned sampling containers. In some cases containers may be purchased pre-preserved from the container supplier. Whether prepared by the laboratory or bought pre-preserved, the grades of the preservatives are at a minimum:

- Hydrochloric Acid – Reagent ACS (Certified VOA Free) or equivalent
- Methanol – Purge and Trap grade
- Nitric Acid – Instra-Analyzed or equivalent
- Sodium Bisulfate – ACS Grade or equivalent
- Sodium Hydroxide – Instra-Analyzed or equivalent
- Sulfuric Acid – Instra-Analyzed or equivalent
- Sodium Thiosulfate – ACS Grade or equivalent
- Sodium Hydroxide/Zinc Acetate – Instra-Analyzed or equivalent
- Hexane – Ultra-RESI-Analyzed®

22.3 DEFINITION OF HOLDING TIME

The date and time of sampling documented on the COC form establishes the day and time zero. As a general rule, when the maximum allowable holding time is expressed in “days” (e.g., 14 days, 28 days), the holding time is based on calendar day measured. Holding times expressed in hours (e.g. 6 hours, 24 hours, etc.) are measured from date and time zero. The first day of holding time ends twenty-four hours after sampling. Holding times for analysis include any necessary reanalysis. However, there are some programs that determine holding time compliance based on the date and specific time of analysis compared to the time of sampling regardless of how long the holding time is. This method of calculating holding time can be accommodated by the laboratory through the Project setup in the LIMS system.

22.3.1 Semi-Volatile - Holding times for sample preparation for semi-volatile organics are measured from the sampling date (and time where applicable) until the day (and time where applicable) solvent contacts the sample. If a sample is to be extracted on the day of expiration, the actual time of extraction must be recorded on the sample preparation worksheet and in the TALs preparation batch. Holding times for analysis are measured from the date (and time where applicable) of initiation of extraction to the time of injection into the gas chromatograph.

22.3.2 Volatiles - Holding times for volatile organics are measured from the date (and time where applicable) of sampling to the date and time of injection into the gas chromatograph. The time of initiation of purging is considered the injection time, but data systems record the start of the chromatographic run rather than the start of purging. Hence, if a sample is so near expiration that the start-of-purging time rather than the chromatographic run time is needed to document the integrity of the sample; the analyst must observe and record the start-of-purging time in an NCM. Extractions, e.g. for high level soils, must be completed in time to allow for analysis to be initiated within the maximum allowable holding time.

22.3.3 Inorganics - For inorganic and metals analysis, the preparation/digestion/distillation and analytical procedure must be completed within the maximum holding time as measured from the sampling date (and time where applicable).

22.4 SAMPLING CONTAINERS, PRESERVATION REQUIREMENTS, HOLDING TIMES

The preservation and holding time criteria specified in the following tables are derived from the source documents for the methods. If method required holding times (this information is in the laboratory SOPs) or preservation requirements are not met, the reports will be qualified using a flag, footnote or case narrative. As soon as possible or “ASAP” is an EPA designation for tests for which rapid analysis is advised, but for which neither EPA nor the laboratory have a basis for a holding time.

22.5 SAMPLE ALIQUOTS / SUBSAMPLING

Taking a representative sub-sample from a container is necessary to ensure that the analytical results are representative of the sample collected in the field. The size of the sample container, the quantity of sample fitted within the container, and the homogeneity of the sample need consideration when sub-sampling for sample preparation. It is the laboratory’s responsibility to take a representative sub-sample or aliquot of the sample provided for analysis. In that regard the following guidelines apply to analysts:

Analysts should handle each sample as if it is potentially dangerous. At a minimum, safety glasses, gloves, and lab coats must be worn when preparing aliquots for analysis. Refer to the laboratory SOP UP-QA-039, *Sample Homogenization and Subsampling Procedures* for further details.

22.5.1 For water samples, before taking each aliquot for analysis, invert the sample container end-over-end three times and immediately pour off the aliquot. Especially when suspended solids are present, adequate mixing of the sample is extremely important.

22.5.2 For solid samples, when volatile organics are not requested, if the solid can be mixed, stir before removing the aliquot. Mix more than is needed for the analysis to be performed (e.g. if 30 g are needed, mix 50-100 g, if 1 g is needed, mix 20 g, etc…).

- If the solid cannot be easily mixed: After thoroughly mixing the sample within the sample container or, for non-organic methods, the sample can be transferred to a wipe bag (or other suitable plastic bag) for manual mixing, a sub-sample from various quadrants and depths of the sample are taken to acquire the required sample weight.

- For soil samples, avoid debris in the sub-sample aliquot as much as possible (e.g. gravel, sticks, roots and grass); note this information in the sample preparation record.

- If the solid is extremely heterogeneous, and the client has given no instructions, utilize the following technique: separate the like materials into groups on a clean surface and take portions of masses from each group, proportional to their contribution to the original sample, to make a composite. Record in detail exactly how the composite was created. For very unusual samples, consult with the Project Manager, QA department or Department Supervisor/Manager.

22.5.3 For solid samples, when volatile organics analysis is requested, the sample should be manipulated as little as possible. In most cases, the sample will arrive already preserved or in an EnCore™ sampler of the correct mass (requiring quick preservation of the entire amount). If the client requests volatiles on a solid sample which has been collected in a jar and is in a common container from which aliquots for other test methods must be taken, login should deliver the container to the volatiles department for preparing a proper aliquot prior to any other aliquots being taken out.

22.5.4 For multiphasic samples, the client should instruct the laboratory as to the intent of the testing and how to handle the sample. If the entire sample is to be accounted for, and the phases do not mix easily with inversion/stirring, such that a representative aliquot can be taken, the analyst should record the percent by volume of each phase. The analysis must be conducted on each phase separately; the final results are combined mathematically, weighting the individual phase results by volume. One exception to this procedure is the situation addressed in the TCLP and SPLP methods for wastes containing free liquids. However, if the leachate and final filtrate are not miscible, it is necessary to combine mathematically the concentrations of the two (or more) solutions by volume.

SECTION 23

HANDLING OF SAMPLES

It is the responsibility of the client to send us representative and/or homogeneous and properly preserved samples of the system from which they are drawn. The laboratory assumes that all multiple sample containers with the same designator/description and bottle type contain a homogeneous, representative sample.

The laboratory provides the appropriate sample containers, required preservative, chain-of-custody (COC) forms, shipping containers, labels, and custody seals. The laboratory also provides trip blanks and analyte-free water for field blanks. Preparation of methanol containers for field preservation of volatile soil samples is available.

Sample management procedures at the laboratory ensure that sample integrity and custody are maintained and documented from sampling/receipt through disposal.

23.1 CHAIN OF CUSTODY (COC)

The COC form is the written documented history of any sample and can be initiated when bottles are sent to the field, or at the time of sampling. This form is completed by the sampling personnel and accompanies the samples to the laboratory where it is received and stored under the laboratory's custody. The purpose of the COC form is to provide a legal written record of the handling of samples from the time of collection until they are received at the laboratory. It also serves as the primary written request for analyses from the client to the laboratory. The COC form acts as a purchase order for analytical services when no other contractual agreement is in effect.

23.1.1 Field Documentation

The information the sampler needs to provide at the time of sampling on the container label is:

- Sample identification
- Date and time
- Preservative

During the sampling process, the COC form is completed and must be legible. This form includes information such as:

- Client name, address, phone number and fax number (if available)
- Project name and/or number
- The sample identification
- Date, time and location of sampling
- Sample collectors name
- The matrix description
- The container description
- The total number of each type of container
- Preservatives used
- Analysis requested
- Requested turnaround time (TAT)
- Any special instructions
- Purchase Order number or billing information (e.g. quote number) if available
- The date and time that each person received or relinquished the sample(s), including their signed name.

When the sampling personnel deliver the samples directly to the laboratory personnel, the samples are stored in a cooler with ice, as applicable, and remain solely in the possession of the client's field technician until the samples are delivered to the laboratory personnel. The sample collector must assure that each container is in his/her physical possession or in his/her view at all times, or stored in such a place and manner to preclude tampering. The field technician relinquishes the samples in writing on the COC form to the sample control personnel at the laboratory or to a laboratory courier. When sampling personnel deliver the samples through a common carrier (Fed-Ex, UPS), the COC relinquished date/time is completed by the field personnel and samples are released to the carrier. Samples are only considered to be received by the laboratory when personnel at the fixed laboratory facility have physical contact with the samples.

Note: Independent couriers are not required to sign the COC form. The COC is usually kept in the sealed sample cooler. The sample receipt log is stored in log-in and it maintains a list of all receipts by date.

23.1.2 Legal / Evidentiary Chain-of-Custody

Samples being tested for litigation may require locked storage and documentation of the time and personnel responsible when the sample was not in storage. This level of documentation is available upon client request and procedures to define these activities are in place and include the following:

- A chain-of-custody document is initiated for each bottle type submitted by the client. The login staff will complete the custody seal, retain the shipping record with the COC and initiate and internal COC for laboratory use.

- The chain of custody is signed each time the sample is stored, removed from storage, or changes hands. The laboratory uses the LIMS ICOC Module for laboratory use by the analysts and the LIMS sample disposal module
- Clients requesting legal internal chain-of-custody documentation receive the completed forms after the analysis is complete.

23.2 SAMPLE RECEIPT

Samples are received at the laboratory by designated sample receiving personnel and a unique laboratory project identification number is assigned. Each sample container shall be assigned a unique sample identification number that is cross-referenced to the client identification number such that traceability of test samples is unambiguous and documented. Each sample container is affixed with a durable sample identification label. Sample acceptance, receipt, tracking and storage procedures are detailed in the laboratory SOP *UP-SR-001*, Sample Receipt: Handling and Processing Procedures and are summarized in the following sections.

Per State and/or Federal Regulation, the client is responsible to ensure that samples are shipped in accordance with DOT/IATA requirements, and that radioactive materials may only be delivered to licensed facilities. Any samples containing (or suspected to contain) Source, Byproduct, or Special Nuclear Material as defined by 10 CFR should be delivered directly to facilities licensed to handle such radioactive material. Natural material or ores containing naturally occurring radionuclides may be delivered to any Eurofins Chicago facility or courier as long as the activity concentration of the material does not exceed 270 pCi/g alpha or 2700 pCi/g beta (49 CFR Part 173).

23.2.1 Laboratory Receipt

When samples arrive at the laboratory, sample receiving personnel inspect the coolers and samples. The integrity of each sample must be determined by comparing sample labels or tags with the COC and by visual checks of the container for possible damage. Any non-conformance, irregularity, or compromised sample receipt must be documented on a Non-Conformance Memo (NCM) in LIMS and brought to the immediate attention of the project manager and the client. The COC, shipping documents, documentation of any non-conformance, irregularity, or compromised sample receipt, record of client contact, and resulting instructions become part of the project record.

23.2.1.1 Inspection of samples include a check for:

- Complete documentation to include sample identification, location, date and time of collection, collector's name, preservation type, sample type and any additional comments concerning the samples.
- Complete sample labels to include unique identification in indelible ink.
- Use of appropriate sample containers (see Section 22)
- Adherence to holding times as specified in the test method and/or summarized in Section 22.
- Adequate sample volume for required analyses (see Section 22).
- Damage or signs of contamination to sample container. Volatile vials are also inspected for headspace.

Refer to Figure 23-1 (Sample Acceptance Policy) and Figure 23-2 (Login Sample Receipt Checklist) for additional details.

23.2.1.2 Check and record the temperature of the samples or temperature blanks within each cooler that require thermal preservation using the IR gun located in the sample Login department.

- Samples shall be deemed acceptable if arrival temperature is just above freezing and less than or equal to 6.0° C (routinely 4°C +/-2). Samples that are hand-delivered immediately after collection may not be at the required temperatures; however, if there is evidence that the chilling process has begun, such as the arrival on ice, the samples shall be considered acceptable. This will be documented on the COC and on the sample receipt checklist (Figure 23-2) in LIMS.
- If the samples were shipped in ice and solid ice is still present and in direct contact with samples, report the samples as "received on ice." Direct contact means samples must be surrounded by ice cubes or crushed ice. Ice present in a plastic bottle or other container does not constitute direct contact.

23.2.1.3 Verify sample preservation as specified in the test method. Check for correct pH as specified in the test method. The results are documented on the sample receipt checklist in TALs. The pH of each individual preserved bottle will be recorded in LIMS in the Job Login on the Receipt/Container tab. In the case of volatiles it is recorded by the analyst after analysis on the sample tracking sheet. Certain analytes are negatively affected by the presence of residual chlorine. BOD/cBOD are checked for chlorine content at the time of analysis. Cyanide, ammonia, and phenolics should be treated immediately upon collection, which is accomplished by providing treatment ampules with the sample bottles for those samples that might be suspected of containing chlorine, such as wastewaters or drinking waters. The chlorine treatment should be confirmed at log-in.

23.2.1.4 After inspecting the samples, the sample receiving personnel sign and date the COC form, make any necessary notes of the samples' conditions and store them in appropriate refrigerators or storage locations.

23.2.1.5 If samples are received without a COC, the laboratory will provide a generic COC form to be completed by the client when the samples are brought to the laboratory. The client is always provided with a copy of the completed COC form for their records.

23.2.1.6 If analyses with short holding times are requested, the dates and times are inspected to ensure that holding times have not already expired. The appropriate laboratory staff is notified when short hold analysis is required.

23.2.1.7 Samples received after normal working hours are left in their coolers and placed in a cold storage location typically Walk-In Cooler #8. The person receiving the samples must record the date and time received, the presence or absence of ice and custody seals, the temperature of samples, presence and type of packing material, and initials.

Any deviations from these checks described in Section 23.2.1 that question the suitability of the sample for analysis, or incomplete documentation as to the tests required will be resolved by consultation with the client. If the sample acceptance policy criteria (Section 23.3) are not met, the laboratory shall either:

- Retain all correspondence and/or records of communications with the client regarding the disposition of rejected samples The project manager may be able to make decisions on samples with prior knowledge from the client, but documentation of acceptable scenarios must be provided and acknowledge by the client, and records of these decisions must be documented, or

- Fully document any decision to proceed with sample analysis that does not meet sample acceptance criteria.

> Note: North Carolina requires that they be notified when samples are processed that do not meet sample acceptance criteria.

Once Sample acceptance is verified, the samples are logged into the TALs according to the laboratory SOP UP-SR-001, Sample Receipt: Handling and Processing Procedures.

23.2.2 Sample Log-in

All samples that are received by the laboratory are logged into the LIMS to allow the laboratory to track and evaluate sample progress in accordance with the laboratory SOP *UP-SR-001*, Sample Receipt: Handling and Processing Procedures. Each group of samples that are logged in together (typically one project from a given client/sampling event) is assigned a unique job number. Within each job, each sampling point (or sample) receives a unique number. Sample numbers are generated sequentially over time, and are not re-assigned. A sample may be composed of more than one bottle since different preservatives may be required to perform all analyses requested. Even if multiple containers are received for a single sample, each container is uniquely identified with a container ID. The LIMS generates sample labels that are attached to each bottle for a given sample.

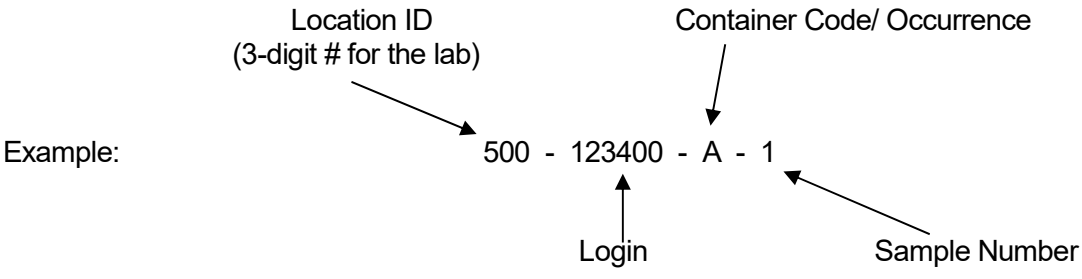
Each job/set of samples is logged into LIMS with a minimum of the following information:

- Client Name, Project Name, Address, Phone, Fax, Report to information, invoice to information (most of this information is “default information” that is stored in the TALs).
- Date and time sampled;
- Date and time received;
- Job and/or project description, sample description;
- Sample matrix, special sample remarks;
- Reporting requirements (i.e., QC level, report format, invoicing format);
- Turn-around-time requirements;
- Parameters (methods and reporting limits or MDLs are default information for a given parameter)

23.2.2.1 Unique Sample Identification

All samples that are processed through the laboratory receive a unique sample identification to ensure that there can be no confusion regarding the identity of such samples at anytime. This system includes identification for all samples, subsamples and subsequent extracts and/or digestates.

The laboratory assigns a unique identification (e.g., Sample ID) code to each sample container received at the laboratory. This Primary ID is made up of the following information (consisting of 4 components):



The above example states that Eurofins Chicago Laboratory (Location 500). Login ID (123400) which is unique to a particular client/job occurrence, the container code (A) indicating the first container of Sample Number (1).

If the primary container goes through a prep step that creates a "new" container, then the new container is considered secondary and gets another ID. An example of this being a client sample in a 1-Liter amber bottle is sent through a Liquid/Liquid Extraction and an extraction vial is created from this step. The vial would be a SECONDARY container. The secondary ID has 5 components.

Example: 500 - 123400 - A - 1 - **A** ← **Secondary Container Occurrence**

Example: 500-123400-A-1-A, would indicate the PRIMARY container listed above that went through a step that created the 1st occurrence of a Secondary container.

With this system, a client sample can literally be tracked throughout the laboratory in every step from receipt to disposal.

23.3 SAMPLE ACCEPTANCE POLICY

The laboratory has a written sample acceptance policy (Figure 23-1) that clearly outlines the circumstances under which samples shall be accepted or rejected. These include:

- a COC filled out completely;
- samples must be properly labeled;
- proper sample containers with adequate volume for the analysis (Sampling Guide) and necessary QC;
- samples must be preserved according to the requirements of the requested analytical method (Sampling Guide);
- sample holding times must be adhered to (Sampling Guide);
- all samples submitted for water/solid Volatile Organic analyses must have a Trip Blank submitted at the same time;
- the project manager will be notified if any sample is received in damaged condition.

Data from samples which do not meet these criteria are flagged and the nature of the variation from policy is defined.

23.4 SAMPLE STORAGE

In order to avoid deterioration, contamination or damage to a sample during storage and handling, from the time of receipt until all analyses are complete, samples are stored in refrigerators, freezers or protected locations suitable for the sample matrix. The metals digestates are stored un-refrigerated in a sample storage closet in the metals instrument lab. In addition, samples to be analyzed for volatile organic parameters are stored in separate refrigerators designated for volatile organic parameters only. Samples are never to be stored with reagents, standards or materials that may create contamination.

To ensure the integrity of the samples during storage, refrigerator blanks are maintained in the volatile sample refrigerators / freezers and are analyzed every two weeks. Refer to laboratory SOP *UP-QA-022, Refrigerated Storage Monitoring –Volatile Samples* for additional details.

Analysts and technicians retrieve the sample container allocated to their analysis from the designated refrigerator and place them on carts, analyze the sample, and return the remaining

sample or empty container to the refrigerator from which it originally came. All unused portions of samples, including empty sample containers, are returned to the secure sample control area. All samples are kept in the refrigerators for four to six weeks after analysis, which meets or exceeds most sample holding times. In general, samples that are not used for validation purposes are retained for 30 days and samples that are being used for validation purposes are retained for 60 days after the final report has been submitted to the client. This holding period allows samples to be checked if a discrepancy or question is raised by the client. Special arrangements may be made to store samples for longer periods of time. This extended holding period allows additional metals analyses to be performed on the archived sample and assists clients in dealing with legal matters or regulatory issues.

Access to the laboratory is controlled such that sample storage need not be locked at all times unless a project specifically demands it. Samples are accessible to laboratory personnel only. Visitors to the laboratory are prohibited from entering the refrigerator and laboratory areas unless accompanied by an employee of Eurofins Chicago.

23.5 HAZARDOUS SAMPLES AND FOREIGN SOILS

To minimize exposure to personnel and to avoid potential accidents, known or found to be hazardous samples may be stored in an isolated area, in a fume hood or with secondary containment. The sample itself is clearly marked with a sample label reading “HAZARDOUS” or “FOREIGN SOIL”. The date, log number, lab sample number, and the result or brief description of the hazard are all written on the bottle. Analysts will notify a Sample Custodian or the Health and Safety Manager of any sample determined to be hazardous after completion of analysis. All hazardous samples are either returned to the client or disposed of appropriately in accordance with current regulations through a hazardous waste disposal firm that lab-packs all hazardous samples and removes them from the laboratory. Foreign soil samples are autoclaved by the laboratory or sent out for incineration by a USDA-approved waste disposal facility.

23.6 SAMPLE SHIPPING

In the event that the laboratory needs to ship samples, the samples are placed in a cooler with enough ice to ensure the samples remain just above freezing and at or below 6.0°C during transit. The samples are carefully surrounded by packing material to avoid breakage (yet maintain appropriate temperature). A trip blank, that which was originally received with the samples, is enclosed for those samples requiring water/solid volatile organic analyses (see Note).. The chain-of-custody form is signed by the sample Login personnel and attached to the shipping paperwork. Samples are generally shipped overnight express or hand-delivered by a Eurofins Chicago courier to maintain sample integrity. All personnel involved with shipping and receiving samples must be trained to maintain the proper chain-of-custody documentation and to keep the samples intact and on ice. The Environmental, Health and Safety Manual contains additional shipping requirements.

Note: If a client does not request trip blank analysis on the COC or other paperwork, the laboratory will not analyze the trip blanks that were supplied. However, in the interest of good client service, the laboratory will advise the client at the time of sample receipt that it was noted that they did not request analysis of the trip blank; and that the laboratory is providing the notification to verify that they are not inadvertently omitting a key part of regulatory compliance testing.

23.7 SAMPLE DISPOSAL

Samples should be retained for a minimum of 30 days after the project report is sent, however, provisions may be made for earlier disposal of samples once the holding time is exceeded. Some samples are required to be held for longer periods based on regulatory or client

requirements (e.g., 60 days after project report is sent). The laboratory must follow the longer sample retention requirements where required by regulation or client agreement. Several possibilities for sample disposal exist: the sample may be consumed completely during analysis, the sample may be returned to the customer or location of sampling for disposal, or the sample may be disposed of in accordance with the laboratory's waste disposal procedures. Refer to SOP *UP-WM-001*, Laboratory Waste Disposal Procedure. All procedures in the laboratory Environmental, Health and Safety Manual are followed during disposal. Samples are normally maintained in the laboratory no longer than three months from receipt unless otherwise requested. Unused portions of samples found or suspected to be hazardous according to state or federal guidelines may be returned to the client upon completion of the analytical work.

If a sample is part of a known litigation, the affected legal authority, sample data user, and/or submitter of the sample must participate in the decision about the sample's disposal. All documentation and correspondence concerning the disposal decision process must be kept on file. Pertinent information includes the date of disposal, nature of disposal (such as sample depletion, hazardous waste facility disposal, or return to client), names of individuals who conducted the arrangements and physically completed the task. The laboratory will remove or deface sample labels prior to disposal unless this is accomplished through the disposal method (e.g., samples are incinerated). A waste disposal record is available in LIMS via the sample disposal module.

Figure 23-1.

Example: Sample Acceptance Policy

Eurofins Chicago Sample Acceptance Policy

Upon receipt of samples at the facility, the laboratory will assess all samples based upon the following criteria. The purpose of such criteria is to maintain the integrity of the samples and ensure that proper sampling and preservation procedures have been followed. Samples found to be in 'non-compliance' with this policy will be formally addressed and conditions documented according to internal operating procedures. Subsequent analysis of such samples may or may not proceed and will be determined by discussion with the appropriate parties involved.

Samples are considered "compromised" if the following conditions are observed upon sample receipt:

- Cooler and/or samples are received outside of temperature specification.
- Samples are received broken or leaking.
- Samples are received beyond holding time.
- Samples are received without appropriate preservation.
- Samples are received in inappropriate containers.
- COC does not match samples received.
- COC is not properly completed or not received.
- Breakage of any Custody Seal.
- Apparent tampering with cooler and/or samples.
- Headspace in volatiles samples.
- Seepage of extraneous water or materials into samples.
- Inadequate sample volume.
- Illegible, impermanent, or non-unique sample labelling.

Refer to the Sample Receipt SOP UP-SR-001 for additional details.

Figure 23-2.

Example: Cooler Receipt Form

LOGIN SAMPLE RECEIPT CHECK LIST

Client:_____Job Number:_____

Login Number:_____
List Number: _____ List Source: _____

Question	Answer	Comment
Radioactivity wasn't checked or is </= background as measured by a survey meter.	Yes	
The cooler's custody seal, if present, is intact	Yes	
Sample custody seals, if present, are intact.	Yes	
The cooler or samples do not appear to have been compromised or tampered with	Yes	
Samples were received on ice.	Yes	3.3, 3.1, 2.7, 2.5
Cooler Temperature is acceptable.	Yes	
Cooler Temperature is recorded.	Yes	
COC is present	Yes	
COC is filled out in ink and legible.	Yes	
COC is filled out with pertinent information.	Yes	
Is the Field Sampler's name present on COC?	Yes	
There are no discrepancies between the containers received and the COC.	Yes	
Samples are received within Holding Time (excluding tests with immediate HTs).	Yes	
Sample containers have legible labels.	Yes	
Containers are not broken or leaking.	Yes	
Sample collection dates/times are provided.	Yes	
Appropriate sample containers are used.	Yes	
Sample bottles are completely filled.	Yes	
Sample Preservation Verified.	Yes	
There is sufficient vol. for all requested analyses including any requested MS/MSDs.	Yes	
Containers requiring zero headspace have no headspace or bubble is < 6mm (1/4").	Yes	
Multiphasis samples are not present	Yes	
Samples do not require splitting or compositing	Yes	
Residual Chlorine Checked	NA	

SECTION 24

ASSURING THE QUALITY OF TEST RESULTS

24.1 OVERVIEW

In order to assure our clients of the validity of their data, the laboratory continuously evaluates the quality of the analytical process. The analytical process is controlled not only by instrument calibration as discussed in Section 20, but also by routine process quality control measurements (e.g. Blanks, Laboratory Control Samples (LCS), Matrix Spikes (MS), duplicates (DUP), surrogates, Internal Standards (IS)). These quality control checks are performed as required by the method or regulations to assess precision and accuracy. Quality control samples are to be treated in the exact same manner as the associated field samples being tested. In addition to the routine process quality control samples, Proficiency Testing (PT) Samples (concentrations unknown to laboratory) are analyzed to help ensure laboratory performance.

24.2 CONTROLS

Sample preparation or pre-treatment is commonly required before analysis. Typical preparation steps include homogenization, grinding, solvent extraction, sonication, acid digestion, distillation, reflux, evaporation, drying and ashing. During these pre-treatment steps, samples are arranged into discreet manageable groups referred to as preparation (prep) batches. Prep batches provide a means to control variability in sample treatment. Control samples are added to each prep batch to monitor method performance and are processed through the entire analytical procedure with investigative/field samples.

24.3 NEGATIVE CONTROLS

Table 24-1. Example – Negative Controls

Control Type	Details
Method Blank (MB)	are used to assess preparation and analysis for possible contamination during the preparation and processing steps.
	The specific frequency of use for method blanks during the analytical sequence is defined in the specific standard operating procedure for each analysis. Generally it is 1 for each batch of samples; not to exceed 20 environmental samples.
	The method blank is prepared from a clean matrix similar to that of the associated samples that is free from target analytes (e.g., Reagent water, Ottawa sand, glass beads, Teflon strips, etc.) and is processed along with and under the same conditions as the associated samples. The method blank goes through all of the steps of the process (including as necessary: filtration, clean-ups, etc.).
	Evaluation criteria and corrective action for method blanks is defined in the specific standard operating procedure for each analysis. Reanalyze or qualify associated sample results when the concentration of a targeted analyte in the blank is at or above the reporting limit as established by the method or by regulation, AND is greater than 1/10 of the amount measured in the sample. Note: Some methods and QAPP specific criteria requires that method blanks be < ½ the reporting limit.
Calibration Blanks	are prepared and analyzed along with calibration standards where applicable. They are prepared using the same reagents that are used to prepare the standards. In some analyses the calibration blank may be included in the calibration curve.

Table 24-1. Example – Negative Controls

Control Type	Details
Instrument Blanks	are blank reagents or reagent water that may be processed during an analytical sequence in order to assess contamination in the analytical system. In general, instrument blanks are used to differentiate between contamination caused by the analytical system and that caused by the sample handling or sample prep process. Instrument blanks may also be inserted throughout the analytical sequence to minimize the effect of carryover from samples with high analyte content.
Trip Blank [1]	are required to be submitted by the client with each shipment of samples requiring aqueous and solid volatiles analyses (or as specified in the client's project plan). Additionally, trip blanks may be prepared and analyzed for volatile analysis of air samples, when required by the client. A trip blank may be purchased (certified clean) or is prepared by the laboratory by filling a clean container with pure deionized water that has been purged to remove any volatile compounds. Appropriate preservatives are also added to the container. The trip blank is sent with the bottle order and is intended to reflect the environment that the containers are subjected to throughout shipping and handling and help identify possible sources if contamination is found. The field sampler returns the trip blank in the cooler with the field samples.
Field Blanks [1]	are sometimes used for specific projects by the field samplers. A field blank prepared in the field by filling a clean container with pure reagent water and appropriate preservative, if any, for the specific sampling activity being undertaken. (EPA OSWER)
Equipment Blanks [1]	are also sometimes created in the field for specific projects. An equipment blank is a sample of analyte-free media which has been used to rinse common sampling equipment to check effectiveness of decontamination procedures. (TNI)
Holding Blanks	also referred to as refrigerator or freezer blanks, are used to monitor the sample storage units for volatile organic compounds during the storage of VOA samples in the laboratory

[1] When known, these field QC samples should not be selected for matrix QC as it does not provide information on the behavior of the target compounds in the field samples. Usually, the client sample ID will provide information to identify the field blanks with labels such as "FB", "EB", or "TB."

Evaluation criteria and corrective action for these controls are defined in the specific standard operating procedure for each analysis.

24.4 POSITIVE CONTROLS

Control samples (e.g., QC indicators) are analyzed with each batch of samples to evaluate data based upon (1) Method Performance (Laboratory Control Sample (LCS) or Blank Spike (BS)), which entails both the preparation and measurement steps; and (2) Matrix Effects (Matrix Spike (MS) or Sample Duplicate (MD, DUP), which evaluates field sampling accuracy, precision, representativeness, interferences, and the effect of the matrix on the method performed. Each regulatory program and each method within those programs specify the control samples that are prepared and/or analyzed with a specific batch

Note that frequency of control samples vary with specific regulatory, methodology and project specific criteria. Complete details on method control samples are as listed in each analytical SOP also refer to Appendix 4 for a listing of the laboratory's default criteria that is followed.

24.4.1 Method Performance Control - Laboratory Control Sample (LCS)

24.4.1.1 The LCS measures the accuracy of the method in a blank matrix and assesses method performance independent of potential field sample matrix affects in a laboratory batch.

24.4.1.2 The LCS is prepared from a clean matrix similar to that of the associated samples that is free from target analytes (for example: Reagent water, Ottawa sand, glass beads, etc.) and is processed along with and under the same conditions as the associated samples. The LCS is spiked with verified known amounts of analytes or is made of a material containing known and verified amounts of analytes, taken through all preparation and analysis steps along

with the field samples. Where there is no preparation taken for an analysis (such as in aqueous volatiles), or when all samples and standards undergo the same preparation and analysis process, a calibration verification standard is reported as the LCS. In some instances where there is no practical clean solid matrix available, aqueous LCS's may be processed for solid matrices; final results may be calculated as mg/kg or ug/kg, assuming 100% solids and a weight equivalent to the aliquot used for the corresponding field samples, to facilitate comparison with the field samples.

24.4.1.3 Certified pre-made reference material purchased from a NIST/A2LA accredited vendor may also be used for the LCS when the material represents the sample matrix or the analyte is not easily spiked (e.g. solid matrix LCS for metals, TDS, etc.).

24.4.1.4 The specific frequency of use for LCS during the analytical sequence is defined in the specific standard operating procedure for each analysis, it is also defined in Appendix 4 (Default Criteria). The frequency is generally 1 for each batch of samples; not to exceed 20 environmental samples.

24.4.1.5 If the mandated or requested test method, or project requirements, do not specify the spiking components, the laboratory shall spike all reportable components to be reported in the Laboratory Control Sample (and Matrix Spike) where applicable (e.g. no spike of pH). However, in cases where the components interfere with accurate assessment (such as simultaneously spiking Chlordane, Toxaphene and PCBs in Method 608), the test method has an extremely long list of components or components are incompatible, at a minimum, a representative number of the listed components (see below) shall be used to control the test method. The selected components of each spiking mix shall represent all chemistries, elution patterns and masses, permit specified analytes and other client requested components. However, the laboratory shall ensure that all reported components are used in the spike mixture within a two-year time period.

- For methods that have 1-10 target analytes, spike all components.
- For methods that include 11-20 target analytes, spike at least 10 or 80%, whichever is greater.
- For methods with more than 20 target analytes, spike at least 16 components.
- Exception: Due to analyte incompatibility in pesticides, separate Toxaphene and Chlordane standards are only spiked at client request based on specific project needs. If required to meet project objectives, separate LCSs can be prepared and analyzed for Toxaphene, Chlordane, or an alternate Aroclor and project specified limits will be applied. The project / job notes in LIMs will be used to identify which projects require the additional LCS spikes.
- Exception: Due to analyte incompatibility between the various PCB aroclors, aroclors 1016 and 1260 are used for spiking as they cover the range of all of the aroclors. Specific aroclors may be used by request on a project specific basis.

24.4.1.6 **<u>Accuracy Calculation</u>**: Percent Recovery (%R) Calculation (applies to LCS, CCV, Surrogates, and Matrix Spikes).

$$\%R = \frac{AV}{TV} \times 100$$

Where: AV = Analyzed Value
TV = True Value

24.5 SAMPLE MATRIX CONTROLS

Table 24-2. Sample Matrix Control

Control Type	Details	
Matrix Spikes (MS)	Use	used to assess the effect sample matrix of the spiked sample has on the precision and accuracy of the results generated by the method used;
	Typical Frequency [1]	At a minimum, with each matrix-specific batch of samples processed, an MS is carried through the complete analytical procedure. Unless specified by the client, samples used for spiking are randomly selected and rotated between different client projects. If the mandated or requested test method does not specify the spiking components, the laboratory shall spike all reportable components to be reported in the Laboratory Control Sample and Matrix Spike. Refer to the method SOP for complete details
	Description	essentially a sample fortified with a known amount of the test analyte(s).
Surrogate	Use	Measures method performance to sample matrix (organics only).
	Typical Frequency [1]	Are added to all samples, standards, and blanks, for all organic chromatography methods except when the matrix precludes its use or when a surrogate is not available. The recovery of the surrogates is compared to the acceptance limits for the specific method. Poor surrogate recovery may indicate a problem with sample composition and shall be reported, with data qualifiers, to the client whose sample produced poor recovery.
	Description	Are similar to matrix spikes except the analytes are compounds with properties that mimic the analyte of interest and are unlikely to be found in environment samples.
Duplicates[2]	Use	For a measure of analytical precision, with each matrix-specific batch of samples processed, a matrix duplicate (MD or DUP) sample, matrix spike duplicate (MSD), or LCS duplicate (LCSD) is carried through the complete analytical procedure.
	Typical Frequency [1]	Duplicate samples are usually analyzed with methods that do not require matrix spike analysis.
	Description	Performed by analyzing two aliquots of the same field sample independently or an additional LCS.
Internal Standards	Use	Are spiked into all environmental and quality control samples (including the initial calibration standards) to monitor the qualitative aspect of organic and some inorganic analytical measurements.
	Typical Frequency [1]	All organic and ICP methods as required by the analytical method.
	Description	Used to correct for matrix effects and to help troubleshoot variability in analytical response and are assessed after data acquisition. Possible sources of poor internal standard response are sample matrix, poor analytical technique or instrument performance.

[1] See the specific analytical SOP for type and frequency of sample matrix control samples.

[2] LCSD's are normally not performed except when regulatory agencies or client specifications require them. The recoveries for the spiked duplicate samples must meet the same laboratory established recovery limits as the accuracy QC samples. If an LCSD is analyzed both the LCS and LCSD must meet the same recovery criteria and be included in the final report. The precision measurement is reported as "Relative Percent Difference" (RPD). Poor precision between duplicates (except LCS/LCSD) may indicate non-homogeneous matrix or sampling.

24.5.1 MS Percent Recovery Calculation is essentially the same as the calculation shown in 24.4.1.6 except that:

AV = Sp – Sa

Where: Sp = Spike result
Sa = Sample result

24.5.2 Precision Calculation (Relative Percent Difference - RPD)

$$RPD = \frac{|S - D|}{\frac{(S + D)}{2}} \times 100$$

Where: S=Sample Concentration
D=Duplicate Concentration

24.6 ACCEPTANCE CRITERIA (CONTROL LIMITS)

24.6.1 As mandated by the test method or regulation, each individual analyte in the LCS, MS, or Surrogate Spike are evaluated against the control limits as published in the test method. Where there are no established acceptance criteria, the laboratory calculates in-house control limits with the use of control charts or, in some cases, utilizes client project specific or regulatory mandated control limits. When this occurs, the regulatory or project limits will supersede the laboratory's in-house limits.

Control charts are monitored to detect trends such as shifts in mean recovery, changes in standard deviation, and to assist in troubleshooting apparent trends. Control charts are also used as a visual aid to help ensure that an appropriate set of data is being selected when setting control limits. More rigorous statistical tests can also be used to determine if different portions of the selected data belong to the same population and may be pooled. For example, the t-test can be used to test means and the F-test can be used to test variances.

Note: For methods, analytes and matrices with very limited data (e.g., unusual matrices not analyzed often), interim limits are established using available data or by analogy to similar methods or matrices.

24.6.2 Once control limits have been established, they are verified, reviewed, and updated if necessary on an annual basis unless the method requires more frequent updating or significant changes to the method or preparation procedure warrant re-evaluation of the limits (e.g. EPA SW846 8000 series methods). Control limits are established per method (as opposed to per instrument) regardless of the number of instruments utilized. Refer to Section 7.6.1 for additional details on control charts.

24.6.3 Laboratory generated % Recovery acceptance (control) limits are generally established by taking $\pm$ 3 Standard Deviations (99% confidence level) from the average recovery of a minimum of 20-30 data points (more points are preferred).

- Regardless of the calculated limit, the limit should be no tighter than the Calibration Verification (ICV/CCV), unless the analytical method specifies a tighter limit.
- In-house limits cannot be any wider than those mandated in a regulated analytical method. Client or contract required control limits are evaluated against the laboratory's statistically derived control limits to determine if the data quality objectives (DQOs) can be achieved. If the laboratory control limits are not consistent with DQOs, then alternatives must be considered, such as method improvements or use of an alternate analytical method.
- The lowest acceptable recovery limit will be 10% and the analyte must be detectable and identifiable.
- The maximum acceptable recovery limit will be 150%.
- The maximum acceptable RPD limit for poor performers will be 35% for waters and 40% for soils.
- The maximum acceptable RPD limit will be 20% for waters and 30% for soils.
- If either the high or low end of the control limit changes by $\leq$ 5% from previous, the control chart is visually inspected and, using professional judgment, they may be left unchanged if there is no effect on laboratory ability to meet the existing limits. Additional statistical tests (e.g., t and F tests) may be applied to the mean and variance to determine if the new data belong to the same population and may be pooled to establish new control limits.

24.6.4 The lab must be able to generate a current listing of their control limits and track when the updates are performed. In addition, the laboratory must be able to recreate historical control limits.

24.6.4.1 The QA department generates a Control Limit Summary table for each method and applicable matrix that contains the precision and accuracy acceptability limits for analyses performed at Eurofins Chicago. This summary includes the date range from which the limits were generated and an approval date. The effective date for the control limits are governed by the date that the limits are entered into the LIMS system. The tables and TALs are updated each time new limits are generated. The current summary tables and any historical limits are located in the \\tacorp\Corp\QA\QA_Facilities\Chicago-QA\Control Limits\STAT directory. Unless otherwise noted, limits within these tables are laboratory generated. The control limits that are entered into LIMS are used by the methods in the evaluation of the data. Each applicable method and matrix is associated with a Method Limit Group in LIMS which houses all applicable limits used by the system in the evaluation of the data. The Quality Assurance department maintains an archive of all limits used within the laboratory.

24.6.5 A LCS that is within the acceptance criteria establishes that the analytical system is in control and is used to validate the process. Samples that are analyzed with an LCS with recoveries outside of the acceptance limits may be determined as out of control and should be reanalyzed if possible. If reanalysis is not possible, then the results for all affected analytes for samples within the same batch must be qualified when reported. The internal corrective action process (see Section 14) is also initiated if an LCS exceeds the acceptance limits. Sample results may be qualified and reported without reanalysis if:

- The analyte results are below the reporting limit and the LCS is above the upper control limit.
- If the analytical results are above the relevant regulatory limit and the LCS is below the lower control limit.

24.6.5.1 The TNI standard allows a number of Marginal Exceedances (ME):

- <11 analytes – 0 marginal exceedances are allowed.
- 11 – 30 Analytes – 1 marginal exceedance is allowed
- 31-50 Analytes – 2 marginal exceedances are allowed
- 51-70 Analytes – 3 marginal exceedances are allowed
- 71-90 Analytes – 4 marginal exceedances are allowed
- > 90 Analytes – 5 marginal exceedances are allowed

- Marginal exceedances are recovery exceedances between 3 SD and 4 SD from the mean recovery limit (TNI).
- Marginal exceedances must be random. If the same analyte exceeds the LCS control limit repeatedly, it is an indication of a systematic problem. The source of the error must be located and corrective action taken. The laboratory has a system to monitor marginal exceedances to ensure that they are random.

Though marginal excedences may be allowed, the data must still be qualified to indicate it is outside of the normal limits.

24.6.6 If the MS/MSDs do not meet acceptance limits, the MS/MSD and the associated spiked sample is reported with a qualifier for those analytes that do not meet limits. If obvious preparation errors are suspected, or if requested by the client, unacceptable MS/MSDs are reprocessed and reanalyzed to prove matrix interference. A more detailed discussion of acceptance criteria and corrective action can be found in Appendix 4 (Default criteria), within the method specific SOPs and in Section 14.

24.6.7 If a surrogate standard falls outside the acceptance limits, if there is not obvious chromatographic matrix interference, reanalyze the sample to confirm a possible matrix effect. If the recoveries confirm or there was obvious chromatographic interference, results are reported from the original analysis and a qualifier is added. If the reanalysis meets surrogate recovery criteria, the second run is reported (or both are reported if requested by the client). Under certain circumstances, where all of the samples are from the same location and share similar chromatography, the reanalysis may be performed on a single sample rather than all of the samples and if the surrogate meets the recovery criteria in the reanalysis, all of the affected samples would require reanalysis. A more detailed discussion of acceptance criteria and corrective action can be found in Appendix 4 (Default criteria) and within the method specific SOPs.

24.7 ADDITIONAL PROCEDURES TO ASSURE QUALITY CONTROL

24.7.1 The laboratory has written and approved method SOPs to assure the accuracy of the test method including calibration (see Section 20), use of certified reference materials (see Section 21) and use of PT samples (see Section 17).

24.7.2 A discussion regarding MDLs, Limit of Detection (LOD) and Limit of Quantitation (LOQ) can be found in Section 19.

24.7.3 Use of formulae to reduce data is discussed in the method standard operating procedures and in Section 19.

24.7.4 Selection of appropriate reagents and standards is included in Section 11 and 21.

24.7.5 A discussion on selectivity of the test is included in Section 7.

24.7.6 Constant and consistent test conditions are discussed in Section 6.

24.7.7 The laboratories sample acceptance policy is included in Section 23.

24.7.8 A listing of the type of test result correlations that are looked at during report review (e.g. TKN should be greater or equal to Ammonia) is included in Section 19.15.4.7.

SECTION 25

REPORTING RESULTS

25.1 OVERVIEW

The results of each test are reported accurately, clearly, unambiguously, and objectively in accordance with State and Federal regulations as well as client requirements. Analytical results are issued in a format that is intended to satisfy customer and laboratory accreditation requirements as well as provide the end user with the information needed to properly evaluate the results. Where there is a conflict between the client requests and laboratory ethics or regulatory requirements the laboratory's ethical and legal requirements are paramount, and an adequate solution will be devised working with the client at the time of project set up. (Refer to section 9 for additional details.)

A variety of report formats are available to meet specific needs.

In cases where a client asks for simplified reports, there must be a written request from the client. There still must be enough information that would show any analyses that were out of conformance (QC out of limits) and there should be a reference to a full report that is made available to the client. Review of reported data is included in Section 19.

25.2 TEST REPORTS

Analytical results are reported in a format that is satisfactory to the client and meets all requirements of applicable accrediting authorities and agencies. A variety of report formats are available to meet specific needs. The report is printed on laboratory letterhead, reviewed, and signed by the appropriate project manager or designee. At a minimum, the standard laboratory report shall contain the following information:

25.2.1 The cover page shall include the laboratory name, address, telephone number.

25.2.2 A report title (e.g., Analytical Report).

25.2.3 A unique identification of the report (e.g. Eurofins Chicago Job ID#) and on each page an identification in order to ensure the page is recognized as part of the report and a clear identification of the end.

Note: Page numbers of report are represented as page # of ##. Where the first number is the page number and the second is the total number of pages.

25.2.4 A copy of the chain of custody (COC).

- Any COCs involved with Subcontracting are included.
- In all cases, the applicable COC is scanned and placed in the shipping and receiving documents folder of the data deliverable for its respective job number and is paginated as an integral part of the report.
- Any additional addenda to the report must be treated in a similar fashion so it is a recognizable part of the report and cannot accidentally get separated from the report (eg. Sampling information).

25.2.5 The name and address of client and a project name/number, if applicable.

25.2.6 Client project manager or other contact

25.2.7 Description and unambiguous identification of the tested sample(s) including the client identification code.

25.2.8 Date of receipt of sample, date and time of collection, and date(s) of test preparation and performance, and time of preparation or analysis if the required holding time for either activity is less than or equal to 72 hours.

25.2.9 Date reported or date of revision, if applicable.

25.2.10 Method of analysis including method code (EPA, Standard Methods, etc).

25.2.11 Reporting limit (RL) or Limit of Quantitation (LOQ).

25.2.12 Method detection limit (MDL) (if requested)

25.2.13 Definition of Data qualifiers and reporting acronyms (e.g. ND).

25.2.14 Sample results.

25.2.15 QC data consisting of method blank, surrogate, LCS, and MS/MSD recoveries and control limits.

25.2.16 Condition of samples at receipt including temperature. This may be accomplished in a narrative or by attaching sample login sheets (Refer to Sec. 25.2.4 – Item 3 regarding

additional addenda). A sample receipt checklist is completed by login personnel, temperatures are documented on the COC and on the checklist and are included as part of the data deliverable to the client.

25.2.17 A statement expressing the validity of the results, that the source methodology was followed and all results were reviewed for error.

25.2.18 A statement to the effect that the results relate only to the items tested and the sample as received by the laboratory, except when information is provided by the client. When data is provided by the client there shall be a clear identification of it, and a disclaimer shall be put in the report when the client supplied data can affect the validity of the test.

25.2.19 A statement that the report shall not be reproduced except in full, without prior express written approval by the laboratory coordinator.

25.2.20 A signature and title of the person(s) accepting responsibility for the content of the report and date of issue. Authorized signatories are qualified Project Managers appointed by the Lab Director.

25.2.21 When TNI accreditation is required, the lab shall certify that the test results meet all requirements of TNI or provide reasons and/or justification if they do not.

25.2.22 Where applicable, a narrative to the report that explains the issue(s) and corrective action(s) taken in the event that a specific accreditation or certification requirement was not met.

25.2.23 When Soil samples are analyzed, a specific identification as to whether soils are reported on a “wet weight” or “dry weight” basis.

25.2.24 Appropriate laboratory certification number for the state of origin of the sample, if applicable.

25.2.25 If only part of the report is provided to the client (client requests some results before all of it is complete), it must be clearly indicated on the report (e.g., *‘Preliminary Report’* is printed across each page of the report), and that a complete report will follow once all of the work has been completed.

25.2.26 Any non-Eurofins subcontracted analysis results are provided as a separate report on the official letterhead of the subcontractor and may be appended to the Eurofins Chicago report in its entirety for submission to the client. All subcontracting is clearly identified on the report as to which laboratory performed a specific analysis.

25.2.27 Certification Summary report, where required, will document that unless otherwise noted, all analytes tested and reported by the laboratory were covered by the noted certifications.

Note: Refer to the NDSC Document No. NDSC-US-IT-QP46227, Electronic Reporting and Signature Policy, for details on internally applying electronic signatures of approval.

25.2.28 Where the laboratory is responsible for the sampling stage, in addition to the requirements listed above, reports containing the results of sampling shall include the following, where necessary for the interpretation of test results:

- the date of sampling;
- unambiguous identification of the material sampled;

- the location of sampling plan and procedures, and deviations, addition to or exclusions from the sample procedures;
- a reference to the sampling plan and procedure, and deviations, additions to or exclusions from the sample procedures;
- details of any environmental conditions during sampling that affect the interpretation of test results;
- information required to evaluate measurement uncertainty for subsequent testing

25.3 REPORTING LEVEL OR REPORT TYPE

The laboratory offers four levels of quality control reporting. Each level, in addition to its own specific requirements, contains all the information provided in the preceding level. The packages provide the following information in addition to the information described above:

- Level I is a report with the features described in Section 25.2 above with the exception that no QC results are reported.
- Level II is a Level I report plus batch QC summary information, including results for the method blank, percent recovery for laboratory control samples and matrix spike samples, the RPD values for all MSD, sample duplicate analyses and surrogate recoveries.
- Level III contains all the information supplied in Level II, supplemented with the presentation of data on CLP-like forms, including relevant tune, internal standard and calibration information. No raw data is provided.
- Level IV is the same as Level III with the addition of all raw supporting data.

In addition to the various levels of QC packaging, the laboratory also provides reports in CD deliverable form. Initial reports may be provided to clients by facsimile, as a .pdf file sent via email or CD, as a hardcopy report or by any combination of the three. Procedures used to ensure client confidentiality are outlined in Section 25.7.

25.4 Electronic Data Deliverables (EDDs)

EDDs are routinely offered as part of Eurofins Chicago's services. Eurofins Chicago offers a variety of EDD formats including Environmental Resources Program Information System (ERPIMS), Environmental Restoration Information System (ERIS), Automated Data Review (ADR), Staged Electronic Data Deliverable (SEDD), EQUIS ™, GISKEY ™ and other State deliverables besides general formats in Dbase ™, Excel ™ and text.

EDD specifications are submitted to an EDD Specialist by the PM or AE for review. The specification undergoes review for contract and LIMS compatibility. Once the facility has committed to providing data in a specific electronic format, the coding of the format may need to be performed. This coding is documented and validated by the IT LIMS staff. The validation of the code is retained by the Corporate IT staff coding the EDD. Changes to the format must be directed by the program or client and approved by the EDD Specialist and Corporate IT LIMS staff.

EDDs shall be subject to a review to ensure their accuracy and completeness. If EDD generation is automated, review may be reduced to periodic screening if the laboratory can demonstrate that it can routinely generate that EDD without errors. Any revisions to the EDD format must be reviewed until it is demonstrated that it can routinely be generated without errors. If the EDD can be reproduced accurately and if all subsequent EDDs can be produced error-free, each EDD does not necessarily require a review. If an EDD checker program is provided to the laboratory then the EDDs will be screened using this tool.

25.5 SUPPLEMENTAL INFORMATION FOR TEST

The lab identifies any unacceptable QC analyses or any other unusual circumstances or observations such as environmental conditions and any non-standard conditions that may have affected the quality of a result. This is typically in the form of a footnote or a qualifier and/or a narrative explaining the discrepancy in the front of the report.

25.5.1 Numeric results with values outside of the calibration range, either high or low are qualified as estimated.

25.5.2 Where quality system requirements are not met, a statement of compliance/non-compliance with requirements and/or specifications is required, including identification of test results derived from any sample that did not meet TNI sample acceptance requirements such as improper container, holding time, or temperature.

25.5.3 Where applicable, a statement on the estimated uncertainty of measurements; information on uncertainty is needed when a client's instructions so require.

When, as requested by the client and agreed to by Eurofins Chicago, the report includes a statement of conformity to specification or standard (see Special Services, Section 9.4), the report shall clearly identify:

- to which results the statement applies,
- which specifications, standard or parts thereof are met or not, and
- the decision rule that was applied (unless the decision rule is inherent in the requested specification or standard, taking into account the level of risk (such as false accept and false reject and statistical assumptions) associated with the decision rule.

25.5.4 Opinions and Interpretations – The test report contains objective information, and generally does not contain subjective information such as opinions and interpretations. If such information is required by the client, the Laboratory Director will determine if a response can be prepared. If so, the Laboratory Director will designate the appropriate member of the management team to prepare a response. The response will be fully documented, and reviewed by the Laboratory Director, before release to the client. There may be additional fees charged to the client at this time, as this is a non-routine function of the laboratory.

Note: Review of data deliverable packages for submittal to regulatory authorities requires responses to non-conforming data concerning potential impact on data quality. This necessitates a limited scope of interpretation, and this work is performed by the Department Manager/Supervisor, PM or QA Department depending on the type of non-conformance. This is the only form of "interpretation" of data that is routinely performed by the laboratory.

When opinions or interpretations are included in the report, the laboratory provides an explanation as to the basis upon which the opinions and interpretations have been made. Opinions and interpretations are clearly noted as such and where applicable, a comment should be added suggesting that the client verify the opinion or interpretation with their regulator.

25.6 ENVIRONMENTAL TESTING OBTAINED FROM SUBCONTRACTORS

If the laboratory is not able to provide the client the requested analysis, the samples would be subcontracted following the procedures outlined in the NDSC Document No. NDSC-US-SUB-SOP94436, Subcontracting.

Data reported from analyses performed by a subcontractor laboratory are clearly identified as such on the analytical report provided to the client. Results from a subcontract laboratory

outside of Eurofins Chicago are reported to the client on the subcontract laboratory's original report stationary and the report includes any accompanying documentation.

25.7 CLIENT CONFIDENTIALITY

The laboratory will ensure the highest standards of quality and integrity of the data and services provided to our clients.

The laboratory is responsible for maintaining in confidence all client information obtained or created. In situations involving the transmission of environmental test results by telephone, facsimile or other electronic means, client confidentiality must be maintained.

The laboratory will not intentionally divulge to any person (other than the client or any other person designated by the client in writing) any information regarding the services provided by the laboratory or any information disclosed to the laboratory by the client. Furthermore, information known to be potentially endangering to national security or an entity's proprietary rights will not be released.

Information about the client obtained from sources other than the client (e.g., complainant, regulators) shall be confidential between client and the laboratory. The source of this information shall be confidential to the laboratory and shall not be shared with the client, unless agreed by the source.

Note: This shall not apply to the extent that the information is required to be disclosed by the laboratory under the compulsion of legal process. The laboratory will, to the extent feasible, provide reasonable notice to the client before disclosing the information.

Note: Authorized representatives of an accrediting authority are permitted to make copies of any analyses or records relevant to the accreditation process, and copies may be removed from the laboratory for purposes of assessment.

25.7.1 Report deliverable formats are discussed with each new client. If a client requests that reports e-mailed, the reports are to meet all requirements of this document.

25.8 FORMAT OF REPORTS

The formats of reports are designed to accommodate each type of environmental test carried out and to minimize the possibility of misunderstanding or misuse.

25.9 AMENDMENTS TO TEST REPORTS

Corrections, additions, or deletions to reports are only made when justification arises through supplemental documentation. Justification is documented using the laboratory's corrective action system (refer to Section 14).

The revised report is retained on the Archive data server, as is the original report. The revised report is stored in the Archive data server under the sample number followed by Rev(1). The revised report will have the word "revised" or "amended" next to the date rather than the word "reported".

When the report is re-issued, a notation of "Revison: 1" is placed on the cover/signature page of the report *or at the top of the narrative page* with a brief explanation of reason for the re-issue and a reference back to the last final report generated. *For Example*: R*eport was revised to*

include toluene in sample NQA1504 per client's request. This final report replaces the final report generated on 1/27/20 at 10:47am.

25.10 POLICIES ON CLIENT REQUESTS FOR AMENDMENTS

25.10.1 Policy on Data Omissions or Reporting Limit Increases

Fundamentally, our policy is simply to not omit previously reported results (including data qualifiers) or to not raise reporting limits and report sample results as ND. This policy has few exceptions. Exceptions are:

- Laboratory error.
- Sample identification is indeterminate (confusion between COC and sample labels).
- An incorrect analysis (not analyte) was requested (e.g., COC lists 8315 but client wanted 8310). A written request for the change is required.
- Incorrect limits reported based on regulatory requirements.
- The requested change has absolutely *no possible* impact on the interpretation of the analytical results and there is *no possibility* of the change being interpreted as misrepresentation by anyone inside or outside of our company.

25.10.2 Multiple Reports

The laboratory does not issue multiple reports for the same work order where there is different information on each report (this does not refer to copies of the same report) unless required to meet regulatory needs and approved by QA.

Appendix 1. List of Governing Documents applicable to the QA Manual
(NDSC, KDG and Laboratory SOPs and Policies)

NDSC Doc. No.	Title
NDSC-US-IT-QP46227	Electronic Reporting and Signature Policy
CA-L-P-002	Contract Compliance Policy
NDSC-QA-QP44940	Calibration Curves and the Selection of Calibration Points
NDSC-QA-SOP46704	Acid and Solvent Testing and Approval Program
NDSC-QA-SOP43862	Manual Integrations
NDSC-QA-SOP42091	Detection and Quantitation Limits
NDSC-QA-SOP-43847	Root Cause Analysis
NDSC-US-EHS-QP46060	NDSC HSE Manual
NDSC-US-IT-QP46202	IT Change Control Procedure Manual
CW-L-P-001	Records Retention Policy
CW-L-WI-001	Records Retention Storage Schedule
SOP01-QA-QP5252	Ethics and Data Integrity Policy
QA-SOP38228	Internal Ethics and Data Integrity Investigation
NDSC-US-SUB-SOP44936	Subcontracting
CED-Q-DC-SOP45894	Document Control and Archiving
CED-Q-DC-SOP45969	Writing a Standard Operating Procedure (SOPs)
NDSC-QA_SOP5260	Internal Auditing
QA-QP38702	Management Systems Review
QA-SOP38229	Nonconforming Work
Local Laboratory Document No.	**Title**
UP-DM-001	Process Operation and Record Retention and Purging
UP-FM-002	EH&S Manual Addendum
UP-FS-001	Field Services; Groundwater Sampling – Bailing Method
UP-IS-006	Proc/Processes Entry, Storage, Backup/Retrieval, Mgmt Bench Data
UP-QA-003	Balance Calibration, Care and Use
UP-QA-014	Training Program: Mechanisms and Documentation Processes Defined by Operational Assessment
UP-QA-017	Method Detection Limits
UP-QA-022	Refrigerated Storage Monitoring Volatile Samples
UP-QA-034	Thermometer Calibrations
UP-QA-039	Sample Homogenization Sub Sampling Procedures
UP-QA-040	Quality Assurance – Measurement Uncertainty
UP-QA-042	Signature Authority & Document Control
UP-SR-001	Sample Receipt: Handling and Processing Procedures
UP-WM-001	Laboratory Waste Disposal Procedures

Appendix 2. References used to prepare the QA Manual

The QAM has been prepared to be consistent with the requirements of the following documents:

- ANSI/ASQC, E4-1994, "Specifications and Guidelines for Quality Management Systems for Environmental Data Collection and Environmental Technology Programs" (American National Standard, January 5, 1995, or most recent version)
- "EPA Requirements for Quality Management Programs" (QA/R-2) (EPA/240/B-01/002, May 31, 2006).
- EPA 600/4-88/039, *Methods for the Determination of Organic Compounds in Drinking Water,* EPA, Revised July 1991.
- EPA 600/R-95/131, *Methods for the Determination of Organic Compounds in Drinking Water,* Supplement III, EPA, August 1995.
- EPA 600/4-79-019, *Handbook for Analytical Quality Control in Water and Wastewater Laboratories,* EPA, March 1979.
- *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996; Final Update IV, January 2008; Final Update V, August 2015.*
- Federal Register, 40 CFR Parts 136, 141, 172, 173, 178, 179 and 261.
- *Manual for the Certification of Laboratories Analyzing Drinking Water (EPA 815-R-05-004, January 2005) (DW labs only)*
- APHA, *Standard Methods for* the Examination of Water and Wastewater, 18th Edition, 19th, 20th, 21st, 22nd and on-line Editions.
- Toxic Substances Control Act (TSCA).
- ISO/IEC Guide 17025: 2017(E)
- The NELAC Institute (TNI) Standard, dated 2016, Volume 1, Modules 1, 2 and 4

Appendix 3. Analytical Method References

Reference methods include: [Delete references below if not used in your lab]

- *Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, August 1980.*
- *Eastern Environmental Radiation Facility Radiochemistry Procedures Manual, EPA, PB84-215581, June 1984.*
- *HASL-300 28th Edition, Environmental Measurements Laboratory (EML), 1997.*
- *Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, Fourth Edition, EPA/600/4-90/027F, August 1993.*
- *Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, Fifth Edition, EPA-821-R-02-012, October 2002.*
- *Analytical Method for Determination of Asbestos Fibers in Water, EPA-600/4-83, September 1983.*
- *Determination of Asbestos Structures Over 10-mm in Length in Drinking Water, EPA-600/R-94-134, June 1994.*
- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, US EPA, January 1996.*
- *Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Analysis and Sampling Procedures; 40CFR Part 136 as amended by Method Update Rule; August 28, 2017.*
- *Methods for Chemical Analysis of Water and Wastes, EPA 600 (4-79-020), 1983.*
- *Methods for the Determination of Inorganic Substances in Environmental Samples, EPA-600/R-93/100, August 1993.*
- *Methods for the Determination of Metals in Environmental Samples, EPA/600/4-91/010, June 1991. Supplement I: EPA-600/R-94/111, May 1994.*
- *Methods for the Determination of Organic Compounds in Drinking Water, EPA-600/4-88-039, December 1988, Revised, July 1991, Supplement I, EPA-600-4-90-020, July 1990, Supplement II, EPA-600/R-92-129, August 1992. Supplement III EPA/600/R-95/131 - August 1995 (EPA 500 Series) (EPA 500 Series methods)*
- *Technical Notes on Drinking Water Methods, EPA-600/R94-173, October 1994*
- *NIOSH Manual of Analytical Methods, 4th ed., August 1994.*
- *Statement of Work for Inorganics & Organics Analysis, SOM and ISM, current versions, USEPA Contract Laboratory Program Multi-media, Multi-concentration.*
- *Standard Methods for the Examination of Water and Wastewater, 18th/19th /20th/ on-line edition; Eaton, A.D. Clesceri, L.S. Greenberg, A.E. Eds; American Water Works Association, Water Pollution Control Federation, American Public Health Association: Washington, D.C.*
- *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996; Final Update IV, January 2008; Final Update V, August 2015.*
- *Annual Book of ASTM Standards, American Society for Testing & Materials (ASTM), Philadelphia, PA.*
- *National Status and Trends Program, National Oceanographic and Atmospheric Administration, Volume I-IV, 1985-1994.*
- *Manual for the Certification of Laboratories Analyzing Drinking Water (EPA 815-R-05-004, January 2005)* ***(DW labs only)***
- *Code of Federal Regulations (CFR) 40, Parts 136, 141, 172, 173, 178, 179 and 261*

Appendix 4: Summary of Calibration and QC Procedures for GC Organics

Method	QC Check	Frequency	Acceptance Criteria[3]	Corrective Action[4]
SW8081A SW8081B SW8082A	Minimum five-point initial calibration for all target analytes[2]	Initial calibration prior to sample analysis. Perform instrument re-calibration once per year minimum.	Linear regression correlation coefficient $r^2 \geq 0.99$, $r \geq 0.995$. RSD of CF ≤ 20%	Correct problem then repeat initial calibration
SW8151A	Initial calibration verification (ICV) must be from a 2nd source	Once immediately following initial calibration	All target analytes within 15% of expected value Within 20% for 8081B/8082A	Correct problem then repeat initial calibration
	Continuing calibration verification (CCV)	Non-IS Methods: Before sample analysis, every 12 hours, and at the end of the analysis sequence. IS Methods: Before sample analysis, every 12 hours or per specified Project QAPP/ Program frequency.	All analytes within 15% of expected value and within the RT Window.	Repeat CCV once, if it again fails criteria, identify and correct problem, repeat initial CCV (re-calibrate if necessary) and re-analyze all samples since last successful CCV.
	Breakdown check (Endrin and DDT)[1]	Before sample analysis	Degradation ≤15% for both Endrin and DDT.	Inlet/column maintenance; repeat breakdown check and re-analyze all samples since last successful breakdown check.
	Method blank	One per analytical prep batch, not to exceed 20 samples in a batch.	No analytes detected RL. Values between the RL and MDL will be evaluated and flagged with a 'J'	Correct problem then re-prep and analyze method blank and all samples processed with the contaminated blank
	LCS for all analytes	One per prep batch, not to exceed 20 samples in a batch.	Statistical Control Limits	Re-prep and analyze the LCS and all samples in the affected analytical batch
	Surrogate(s)	Every sample, spike, standard, and method blank	Statistical Control Limits	Check system, re-inject, re-extract
	MS/MSD	One per batch per matrix, if insufficient sample for MS/MSD, then a LCS/LCSD will be analyzed.	Statistical Control Limits	None (LCS is used to determine if data is acceptable).
	Second-column confirmation	100% for all positive results	Same as for initial or primary column analysis	Same as for initial or primary column analysis. If the relative % difference of results between the 2 columns is greater than 40%, a comment should be placed in LIMS. Refer to NDSC Doc No. NDSC-QA-QP43869 for additional details.
	Retention time window calculated for each analyte (see section 9 for how to calculate RTWs).	System set-up, with each new column or major instrument maintenance. Update the mid-RTW at the start of the run or daily. (as needed)	Each analyte of the LCS, MS/MSD and CCV must be within the calculated RTW.	Correct the problem and re-process or re-analyze samples. If questions, see the supervisor or technical director.
	MDL verification	Minimum – yearly	Detectible	Re-evaluate MDL standard used and MDL
	Internal Standards	Every sample/standard and blank	RT ±30 seconds from RT of the mid-point std. in the CCV/ICAL (sample/standard). IS area within -50% to +100% of ICAL mid-point std for the CCV & samples.	Refer to corrective action section of method SOP.

1 --8081A/8081B; 2 – Method 8082, a five-point calibration is only analyzed for Aroclors 1016 and 1260 unless specified in program or project QAPP.
3 - This is a summary of the acceptance criteria, refer to the method SOP for specific or more information; 4 - All abnormalities must be noted on the data, the bench sheet and in LIMS.

Appendix 4: Summary of Calibration and QC Procedures for GC Organics

Method	QC Check	Frequency	Acceptance Criteria[3]	Corrective Action[4]
EPA608 608.3	Minimum three-point (preferably five) initial calibration for all target analytes	Initial calibration prior to sample analysis. Perform instrument re-calibration once per year minimum.	**608: RSD of CF ≤ 10%** 608.3: RSD <15% or RSE <15% Linear regression - correlation coefficient $r^2 > 0.990$, $r \geq 0.995$.	Correct problem then repeat initial calibration
	Initial calibration verification (ICV) must be from a 2nd source.	Immediately following initial calibration	All analytes within 15% of expected value	Correct problem then repeat initial calibration
	Continuing calibration verification (CCV)	Before sample analysis, after every 10 samples, and at the end of the analysis sequence.	All analytes within **15% of expected value** and within the RTW.	Repeat CCV once, if it again fails criteria, identify and correct problem, repeat initial CCV (re-calibrate if necessary) and re-analyze all samples since last successful CCV.
	Breakdown check (Endrin and DDT)	Before sample analysis	Degradation ≤15% for both Endrin and DDT.	Inlet/column maintenance; repeat breakdown check and re-analyze all samples since last successful breakdown check.
	Method blank	608: 1 / 10 samples 608.3: 1 / 20 samples	No analytes detected ≥ RL values between the RL and MDL will be evaluated and flagged with a 'J'	Correct problem then re-prep and analyze method blank and all samples processed with the contaminated blank
	LCS (QC check standard)	608: 1 / 10 samples 608.3: 1 / 20 samples	Method Control Limits	Re-prep[7] and analyze the LCS and all samples in the affected analytical batch
	Surrogate(s)	Every sample, spiked sample, standard, and method blank	Method Control Limits	Check system, re-inject, re-extract
	MS	608: 1 MS / 10 samples 608.3: 1 MS/MSD / 20 samples If insufficient sample for MS, then an additional LCS will be analyzed.	Method Control Limits	All target compounds should be reported, and any compounds that are outside criteria must be within criteria in the LCS.
	Second-column confirmation	100% for all positive results	Same as for initial or primary column analysis	Same as for initial or primary column analysis. If the relative % difference of results between the 2 columns is greater than 40%, a comment should be placed in LIMS.
	Retention time window calculated for each analyte (see section 9 for how to calculate RTWs).	System set-up, with each new column or major instrument maintenance. Update the mid-RTW at the start of the run or as needed.	Each analyte of the LCS, MS/MSD and CCV must be within the calculated RTW.	Correct the problem and re-process or re-analyze samples. If questions, see the supervisor or technical director.
	Internal Standards	Every sample/standard and blank	RT ±30 seconds from RT of the mid-point std. in the CCV/ICAL (sample/standard). IS area within -50% to +100% of ICAL mid-point std for the CCV & samples.	Refer to corrective action section of method SOP.
	MDL verification	Minimum yearly	Detectible	Re-evaluate standard used and MDL

3 - This is a summary of the acceptance criteria, refer to the method SOP for specific or more information.
4 - All abnormalities must be noted on the data, the benchsheet and in LIMS.

Appendix 4: Summary of Calibration and QC Procedures for GC/MS Organics

Method	QC Check	Frequency	Acceptance Criteria[2]	Corrective Action[3]
SW8260B/D SW8270C SW8270D/E	Check of mass spectral ion intensities[1], i.e., Tune	Prior to initial calibration or Continuing calibration verification, every 12 hours	Refer to criteria listed in the method SOP for Tune criteria, including DDT, Benzidine and Pentachlorophenol requirements for 8270.	Retune the instrument and verify (instrument maintenance may be needed).
SW8260B/D	Minimum five-point initial calibration for all target analytes	Initial calibration prior to sample analysis. Perform instrument re-calibration as necessary and after major instrument maintenance.	SPCCs average RF ≥ 0.30 or 0.1 depending on the compound and %RSD for RFs for CCCs ≤ 30% and all other target analytes Note: 8260D min RF's are used for guidance only.	Correct problem then repeat initial calibration
SW8270C			SPCCs average RF ≥ 0.050 and %RSD for RFs for CCCs ≤ 30%	Correct problem then repeat initial calibration
			option (if %RSD is > 15%)–linear regression $r^2 \geq 0.990$, $r \geq 0.995$.	Refer to individual SOP for corrective action procedure.
SW8270D			All analytes < 20% RSD, up to 10% of analytes can be > 20% RSD Most analytes must meet minimum RF's (see Table 4 in 8270D SOP) Note: 8270E min RF's are used for guidance only.	Correct problem then repeat initial calibration
SW8260B/D SW8270C SW8270D/E	Initial calibration verification (ICV) must be from a 2nd source.	Immediately following five-point (minimum) initial calibration and before samples are analyzed.	All analytes within 30% of expected value	Correct problem then repeat ICV, if criteria fails it may be necessary to repeat initial calibration or report outlier with PM/QA approval and qualification (NCM required).
	Relative Retention time window	Each sample	Relative retention time (RRT) of the analyte within 0.06 RRT units of the RRT of the internal standard	Correct problem then reprocess or re-analyze all samples analyzed since the last retention time check
SW8260B/D	Continuing calibration verification (CCV)	Daily, before sample analysis and every 12 hours of analysis time	SPCCs average RF ≥ 0.30 or 0.1 depending on the compound; and Note: SW8260D min RF's are used for guidance only.	Correct problem then repeat CCV, if criteria is met, repeat associated samples. If criteria are not met, it may be necessary to repeat initial calibration and re-analyze all samples since last successful CCV.
SW8270C			SPCCs average RF ≥ 0.050; and	
SW8260B SW8270C			CCCs: ≤20% difference (when using RFs) or drift (when using least squares regression).	
SW8260D			All analytes < 20% RSD, up to 10% of analytes can be > 20% RSD (See Table 3 in 8260D SOP for min RF's) Note: 8260D min RF's are used for guidance only.	

Method	QC Check	Frequency	Acceptance Criteria[2]	Corrective Action[3]
SW8270D/E	Continuing calibration verification (CCV)	Daily, before sample analysis and every 12 hours of analysis time	All analytes < 20% RSD, up to 10% of analytes can be > 20% RSD Most analytes must meet minimum RF's (see Table 4 in 8270D/E SOP) Note: 8270E min RF's are used for guidance only.	
SW8260B/D SW8270C SW8270D/E	Method blank	One per analytical prep batch	No analytes detected ≥ RL values between the RL and MDL will be evaluated and flagged with a 'J' ; (Common lab contaminants cited in SOP < 3x RL)	Correct problem then re-prep and analyze MB and all samples processed with the contaminated blank. Common lab contaminants < 3x RL will be narrated.
SW8260B/D SW8270C	Internal Standards	Every sample/standard and blank	Retention time ±30 seconds from retention time of the mid-point std. in the CCV/ICAL (sample/standard). IS area within -50% to +100% of ICAL mid-point std for the CCV and samples.	Refer to corrective action section of method SOP.
SW8270D/E	Internal Standards	Every sample/standard and blank	Retention time ±30 seconds from retention time of the mid-point std. in the CCV/ICAL (sample/standard). IS area within -50% to +100% of ICAL mid-point standard Area based on CCV	Refer to corrective action section of method SOP.
SW8260B/D SW8270C SW8270D/E	LCS for all target analytes	Volatiles: one per tune per 12 hour sequence. Semivolatiles: One per prep batch, not to exceed the 20 samples in a batch.	Statistical Control Limits	Refer to corrective action section of method SOP.
	MS/MSD	One set per batch of 20 samples per matrix, if insufficient sample for MS/MSD, then a LCS/LCSD will be analyzed.	Statistical Control Limits	None (the LCS is used to evaluate and determine if the batch is acceptable).
	Surrogate(s)	Every sample, spike, standard, and blank	Statistical Control Limits	Refer to corrective action section of method SOP.
SW8260B/D	pH check	All 8260 water samples All low level 5035 soils are prepped in sodium sulfate (refer to the method SOP for exceptions).	pH ≤2.	If the pH is > 2, then comment in LIMS via an NCM
All	MDL verification	Minimum – yearly	Detectible	Re-evaluate Standard used and MDL;

1 – SW8260B requires BFB; SW8260D only requires BFB before ICAL; SW8270C and SW8270D requires DFTPP; SW8270E only requires DFTPP before ICAL
2 - This is a summary of the acceptance criteria, refer to the method SOP for specific or more information.
3 - All abnormalities must be noted on the data, the bench sheet and in LIMS.

Appendix 4: Summary of Calibration and QC Procedures for GC/MS Organics

Method	QC Check	Frequency	Acceptance Criteria[1]	Corrective Action[2]
EPA624 624.1 EPA625 625.1	Check of mass spectral ion intensities (i.e. Tune) 624-BFB; 625-DFTPP	Prior to initial calibration or Continuing calibration verification every 24 hours (624/625) every 12 hours (624.1/625.1)	Refer to criteria listed in the method SOP for Tune requirements including DDT, Benzidine and Pentachlorophenol criteria for 625.	Retune instrument and verify instrument maintenance may be needed.
	625 Min 3 pt. calibration 625.1: Min 5 pt. calibration. 624: Min 4 pt. calibration 624.1: Min 5 pt. calibration	Initial calibration prior to sample analysis. Perform instrument re-calibration once per year minimum.	%RSD < 35%	If the calibration is not considered linear by %RSD, then correct problem then repeat initial calibration
	Relative Retention time window	Each sample	Retention time (RT) of the analyte within 30 seconds of the RT (± 0.25 min. RTW is used) of the target.	Correct problem then reprocess or re-analyze all samples analyzed since the last retention time check
	Continuing calibration verification (CCV)	Daily, before sample analysis	All calibration analytes within “Range of Q” of expected value. (Method Control Limits)	Correct problem then repeat initial calibration and re-analyze all samples since last successful CCV.
	Method blank	624: One per tune 625:One per prep batch (not to exceed 20 samples per batch).	No analytes detected ≥ RL. Values between the RL and MDL will be evaluated & flagged with a ‘J’; (Common lab contaminants cited in SOP < 3x RL)	Correct problem then re-prep and analyze method blank and all samples processed with the contaminated blank. Common lab contaminants < 3x RL will be narrated.
	LCS for all analytes in method specified spike list.	624: One per tune 625: One per prep batch (not to exceed 20 samples per batch)	Method Control Limits (Range of P)	Refer to the corrective action section of the Method SOP
	MS for all analytes in method specified spike list.	One per batch of 20 per matrix, if insufficient sample for MS, then a duplicate LCS will be analyzed.	Method Control Limits (Range of P)	None (the LCS is used to evaluate and determine if the batch is acceptable).
	Surrogate(s)	Every sample, spiked sample, standard, and method blank	Statistical Control Limits	Refer to the corrective action section of the Method SOP
	Internal Standards	Every sample/standard	Retention time ±30 seconds from retention time of the mid-point std. in the CCV/ICAL (sample/standard). IS area within -50% to +100% of ICAL mid-point std for the CCV and –50% to +100% of the prior CCV for the samples.	Refer to the corrective action section of the Method SOP
EPA624 624.1	pH check	All 624 samples	pH should be ≤ 2. (Unless un-preserved samples are received.)	If the pH is > 2, then comment in LIMS via an NCM.
EPA624 624.1	Residual chlorine check (NC samples or samples suspected of coming from a chlorinated waste stream)	All samples from NC or a suspected chlorinated waste stream.	Residual chlorine should be negative.	If the residual chlorine is positive, then comment in LIMS via and NCM..
	MDL verification	Minimum yearly	Detectible	Re-evaluate standard used and MDL

1 - This is a summary of the acceptance criteria, refer to the method SOP for specific or more information.
2 - All abnormalities must be noted on the data, the bench sheet and in LIMS.

Appendix 4: Summary of Calibration and QC Procedures for GC Organics

Method	QC Check	Frequency	Acceptance Criteria[1]	Corrective Action[2]
SW8015B[3] SW8015C SW8015D	Minimum five-point initial calibration for all target analytes	Initial calibration prior to sample analysis. Perform instrument re-calibration once per year minimum.	RSD of CF ≤ 20% Linear – least squares regression $r^2 \geq 0.990$, $r \geq 0.995$	Correct problem then repeat initial calibration
	Initial calibration verification (ICV), must be from a 2nd source.	Immediately following five-point initial calibration	All analytes within 15% of expected value Within 20% for 8015C/8015D	Correct problem then repeat initial calibration
	LCS for all analytes	One per prep batch, not to exceed 20 samples in a batch.	Statistical Control Limits	Re-prep and analyze the LCS and all samples in the affected analytical batch
	Continuing calibration verification (CCV)	Before sample analysis, after every 10 samples, and at the end of the analysis sequence	All analytes within 15% of expected value and within the RTW. Within 20% for 8015C/8015D	Repeat CCV, if criteria fails, correct problem then repeat initial CCV (re-calibrate if necessary) and re-analyze all samples since last successful CCV.
	Method blank	One per analytical prep batch, not to exceed 20 samples in a batch.	No analytes detected ≥ RL values between the RL and MDL will be evaluated and flagged with a 'J'	Correct problem then re-prep and analyze method blank and all samples processed with the contaminated blank
	Surrogate	Every sample, spiked sample, standard, and method blank	Statistical Control Limits	Check system, re-analyze, re-prep
	MS/MSD	One per batch per matrix, if insufficient sample for MS/MSD, then a LCS/LCSD will be analyzed.	Statistical Control Limits	None (LCS is used to determine if data is acceptable).
	Retention time window calculated for each analyte (see section 9 for how to calculate RTWs).	System set-up, with each new column or major instrument maintenance. Update the mid-RTW as the start of the run or daily. (as needed)	Each analyte of the LCS, MS/MSD and CCV must be within the calculated RTW.	Correct the problem and re-process or re-analyze samples. For questions, see the supervisor or technical director.
	MDL verification	Minimum yearly	Detectible	Re-evaluate MDL standard used and MDL
SW8015B SW8015C SW8015D – GRO	pH Check	All water samples after analysis.	pH should be less than 2.	If pH is > 2, then place a comment on the bench sheet and in LIMS via an NCM.

1 - This is a summary of the acceptance criteria, refer to the method SOP for specific or more information.
2 - All abnormalities must be noted on the data, the bench sheet and in LIMS.
3 - For GRO and DRO, see state specific SOP/Method for acceptance criteria. If there is not a specific method for that state, then follow the acceptance criteria in this table.

Appendix 4: Summary of Calibration and QC Procedures for Method SW6010B / SW6010C / 6010D

Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SW6010B SW6010C SW6010D	Initial calibration (one to three standards for each element- and a blank)	Daily initial calibration prior to sample analysis.	>/= 0.995 (6010B/6010D) >/= 0.998 (6010C)	Re-calibrate
	Curve high-standards read-back S1 / S2 6010B/6010C	Daily after curve	+/- 5% of known concentration	Re-calibrate, re-run samples for affected elements
	Linear Range Check Standard 6010D	Daily after curve	+/- 10% of known concentration	If LRC fails, sample concentrations can not exceed the high standard of the curve.
	Second-source calibration verification (ICV)	Daily after initial calibration	All analytes within 10% of expected value	Correct problem then repeat initial calibration; may report non-detects if biased high.
	Second-source calibration verification – Low Level (ICVL) 6010C / 6010D	Daily after mid-range ICV (Conc. = RL Level)	All analytes +/-30% (6010C) +/- 20% (6010D) of expected value	Correct problem then repeat initial calibration; may report non-detects if biased high.
	Initial Calibration blank (ICB)	After ICV	+/- RL (6010B / 6010C) +/- ½ RL (6010D)	Correct problem then re-analyze for affected elements; may report results >10X contamination level or non-detects if biased high
	CRI (2X RL)	At the beginning of an analytical run	50-150%	NA
	MRL (at RL)	At the beginning of an analytical run	70-130% (Project Specific)	Per QAPP
	Interference check solution (ICSA) 6010B/6010C/6010D	At the beginning of an analytical run	+/- 20% of expected value of spiked elements. Non-spiked elements: +/- RL	Correct problem; re-analyze ICSA; re-analyze all affected samples; may report non-detects if biased high.
	Interference check solution (ICSB) 6010B / 6010C	At the beginning of an analytical run	+/- 20% of expected value of spiked elements. Non-spiked elements: +/- RL	Correct problem; re-analyze ICSB; re-analyze all affected samples; may report non-detects if biased high.
	Method Blank	One per prep batch of </= 20 samples	+/- RL < /2 RL per QAPP	Correct problem, re-prep and re-analyze the method blank and all samples for affected elements; may report results >10X contamination level or non-detects if biased high
	LCS	One per prep batch of </= 20 samples	+/- 20% of known concentration	Correct problem, then re-prep and analyze the LCS and all samples for affected elements; may report non-detects if biased high.
	Method duplicate	One per prep batch per matrix upon request	</= 20 RPD	Repeat
	MS/MSD	One per prep batch per matrix	+/- 25% of known concentration	None
	Dilution test (SD)	Each new sample matrix	5x dilution must agree within 10% (6010B / 6010C); 20% (6010D) of the original determination	Perform post digestion spike addition upon request

Method 6010B 6010C 6010D	QC Check	Frequency	Acceptance Criteria	Corrective Action
	Post digestion spike addition (PDS)	When dilution test fails for some programs	Recovery within 25% of expected results	None
	Continuing Calibration Verification (CCV)	After every 10 readings and at the end of the analytical sequence	All analytes within 10% of expected value	Correct problem and re-analyze affected elements of bracketed samples; may report non-detects if biased high.
	Second-source calibration verification – Low Level (CCVL) 6010C only	After mid-range CCV (Conc. = RL Level)	All analytes within 30% of expected value	Correct problem and re-analyze affected elements of bracketed samples; may report non-detects if biased high.
	Continuing Calibration blank (CCB)	After each CCV	+/- RL	Correct problem and re-analyze affected elements of bracketed samples; may report results >10X contamination level or non-detects if biased high
	Internal Standard	All samples and QC	50 – 150%	Re-analyze sample at a dilution
	MDL verification	Minimum yearly	Detectible	Re-evaluate standard used and MDL

Appendix 4: Summary of Calibration and QC Procedures for Method SW6020A / 6020B

Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SW6020A SW6020B	Initial calibration (one to three standards for each element- and a blank)	Daily initial calibration prior to sample analysis.	r >/= 0.998 (6020A) r >/= 0.995 (6020B)	Re-calibrate
	Curve high-standards read-back S1 6020A / 6020B	Daily after curve	+/- 5% of known concentration	Re-calibrate, re-run samples for affected elements
	Linear Range Check Standard 6020B	Daily after curve	+/- 10% of know concentration	If LRC fails, sample concentrations can not exceed the high standard of the curve.
	Second-source calibration verification (ICV)	Daily after initial calibration	All analytes within 10% of expected value	Correct problem then repeat initial calibration; may report non-detects if biased high.
	Second-source calibration verification – Low Level (ICVL) 6020A / 6020B	Daily after mid-range ICV/ICB (Conc. = RL Level)	All analytes within 30% of expected value	Correct problem then repeat initial calibration; may report non-detects if biased high.
	Initial Calibration blank (ICB)	After ICV	+/- RL (6020A) +/- ½ RL(6020B)	Correct problem then re-analyze for affected elements; may report results >10X contamination level or non-detects if biased high
	CRI (2X RL)	At the beginning of an analytical run	50-150%	NA
	MRL (at RL)	At the beginning of an analytical run	70 – 130% (Project Specific)	Per QAPP
	Interference check solution (ICSA) 6020A / 6020B	At the beginning of an analytical run and every 12 hours	+/- 20% of expected value of spiked elements. Non-spiked elements: +/- RL	Correct problem; re-analyze ICSA; re-analyze all affected samples; may report non-detects if biased high.
	Interference check solution (ICSB) 6020A	At the beginning of an analytical run and every 12 hours	+/- 20% of expected value of spiked elements. Non-spiked elements: +/- RL	Correct problem; re-analyze ICSB; re-analyze all affected samples; may report non-detects if biased high.
	Method Blank	One per prep batch of </= 20 samples	+/- RL < ½ RL per QAPP	Correct problem, re-prep and re-analyze the method blank and all samples for affected elements; may report results >10X contamination level or non-detects if biased high
	LCS	One per prep batch of </= 20 samples	+/- 20% of known concentration	Correct problem, then re-prep and analyze the LCS and all samples for affected elements; may report non-detects if biased high.
	Method duplicate	One per prep batch per matrix upon request	</= 20 RPD	Repeat
	MS/MSD	One per prep batch per matrix	+/- 25% of known concentration	None
	Dilution test (SD)	Each new sample matrix	5x dilution must agree within 10% (6020A); 20% (6020B) of the original determination	Perform post digestion spike addition upon request

Method cont.	QC Check	Frequency	Acceptance Criteria	Corrective Action
SW6020A SW6020B	Post digestion spike addition (PDS)	When dilution test fails for some programs	Recovery within 25% of expected results	None
	Continuing Calibration Verification (CCV)	After every 10 readings and at the end of the analytical sequence	All analytes within 10% of expected value	Correct problem and re-analyze affected elements of bracketed samples; may report non-detects if biased high.
	Second-source calibration verification – Low Level (CCVL) 6020A	After mid-range CCV/CCB (Conc. = RL Level)	All analytes within 30% of expected value	Correct problem and re-analyze affected elements of bracketed samples; may report non-detects if biased high.
	Continuing Calibration blank (CCB)	After each CCV	+/- RL	Correct problem and re-analyze affected elements of bracketed samples; may report results >10X contamination level or non-detects if biased high
	Internal Standard	All samples and QC	30 – 150%	Re-analyze sample at a dilution
	MDL verification	Minimum yearly	Detectible	Re-evaluate standard used and MDL

Appendix 4: Summary of Calibration and QC Procedures for Method SW7196A

Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SW7196A	Initial calibration (5 standards and a blank)	Initial calibration prior to sample analysis.	r ≥ 0.995	Correct problem then repeat initial calibration
	Second-source calibration verification (ICV)	Immediately following initial calibration	All analytes within 10% of expected value	Correct problem then repeat initial calibration; may report non-detects if biased high.
	Initial Calibration Blank (ICB)	After ICV	+/- RL	Correct problem then proceed; may report results >10X contamination level or non-detects if biased high
	Method blank	One per batch of 10 samples - waters One per batch of 20 samples - solis	+/- RL < ½ RL per QAPP	Correct problem then re-prep and analyze method blank and all samples processed with the contaminated blank. may report results >10X contamination level or non-detects if biased high
	LCS - soluble	One per batch of 10 samples - waters One per batch of 20 samples - solis	+/- 20% of known conc. (3060A prep) +/- 15% of known conc. (waters)	Re-prep, re-analyze all affected samples. ; may report non-detects if biased high.
	LCS – insoluble (3060A soil prep)	One per batch of 20 samples	+/- 20% of known conc. (3060A prep)	Re-prep, re-analyze all affected samples. ; may report non-detects if biased high.
	Matrix duplicate	One per batch upon request	</= 20 RPD	Repeat once
	MS/MSD - soluble	One pair per 10 samples - waters One pair per 20 samples - soils	+/- 25% of known conc. (3060A prep) +/- 15% of know conc. (waters)	Persistent interference indicates the need to evaluate matrix further for reducing agents.
	MS/MSD – insoluble (3060A soil prep)	One pair per batch of 20 samples	+/- 25% of known conc. (3060A prep)	Persistent interference indicates the need to evaluate matrix further for reducing agents.
	Post Digestion Spike (3060A soil prep)	One per batch of 20 samples	+/- 15% of known conc. (3060A prep)	If check indicates interference, dilute and re-analyze sample. Persistent interference indicates the need to evaluate matrix further for reducing agents.
	Continuing calibration verification (CCV)	Beginning and after every 10 samples and at the end of the analysis sequence	All analytes within 10% of expected value	Correct problem and re-analyze all samples since last successful calibration; may report non-detects if biased high.
	Continuing Calibration Blank (CCB)	After every CCV	+/- RL	Correct problem and re-analyze all samples since last successful calibration. May report results >10X contamination level or non-detects if biased high

Appendix 4: Summary of Calibration and QC Procedures for Method SW7470A / SW7471B

Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SW7470A SW7471B	Calibration curve – minimum 5 standards and blank	Quarterly, monthly, or daily – see individual SOP	r ≥ 0.995	Recalibrate
	Initial Calibration Verification – mid-level, second-source required (ICV)	Immediately following initial calibration and daily at the beginning of each analytical sequence.	±10% of known concentration	Correct problem then repeat initial calibration; may report non-detects if biased high.
	Initial Calibration Blank (ICB)	After ICV	+/- RL	Correct problem then proceed; may report results >10X contamination level or non-detects if biased high
	Method blank	One per batch of 20 or fewer samples	+/- RL < ½ RL per QAPP	Correct problem then re-prep and analyze method blank and all samples processed with the contaminated blank. may report results >10X contamination level or non-detects if biased high
	CRA (at RL level)	One per batch of 20 or fewer samples	No established limits	None
	LCS	One per batch of 20 or fewer samples	+/- 20% of known concentration	Correct problem, re-prep and repeat LCS, MB and all samples in the batch; may report non-detects if the LCS is biased high.
	Matrix duplicate	One per matrix per batch of 20 or fewer samples as requested	</= 20 RPD	Repeat once
	MS/MSD	One pair per matrix per batch of 20 or fewer samples	+/- 25% of known concentration	None
	Continuing calibration verification (CCV)	Beginning, every 10 samples, and at end of sequence	±20% of known concentration	Correct problem then repeat CCV, CCB and all samples since last successful CCB; may report non-detects if biased high.
	Continuing Calibration Blank (CCB)	After every CCV	+/- RL	Correct problem then repeat CCV,CCB and all samples since last successful CCB; may report results >10X contamination level or non-detects if biased high
	MDL verification	Minimum yearly	Detectible	Re-evaluate standard used and MDL

Appendix 4: Summary of Calibration and QC Procedures for Cyanide

Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SW9010C 9012B 335.4	Initial calibration (6 standards (9014); 7 standards (9012B; 4500CNE) and a calibration blank)	Initial daily calibration prior to sample analysis.	r ≥ 0.995 y-intercept < abs. value of RL	Correct problem then repeat initial calibration
	Distilled standards 9010B / 9010C (one high and one low)	Once per calibration – Only when curve is not distilled	+/- 10% of known concentration (high) +/- 25% of known concentration (low)	Correct problem then repeat distilled standards and related samples
	Second-source calibration verification (ICV)	Immediately following initial daily calibration	+/- 10% of known concentration	Correct problem. Repeat, then repeat initial calibration if necessary
	Initial Calibration Blank (ICB)	Following ICV	+/- RL	Correct problem. Repeat, then repeat initial calibration, ICV and ICB if necessary; may report non-detects if CCV is biased high
	Method blank	One per prep batch of 20 or fewer samples	+/- RL < ½ RL per QAPP	Correct problem then re-prep and analyze method blank and all samples processed with the contaminated blank; may report non-detects and results >10X the contamination level.
	LCS	One per prep batch of 20 or fewer samples	+/- 15% of known concentration +/- 10% for Drinking Waters	Re-prep, re-analyze affected samples; may report non-detects if biased high
	Matrix duplicate (optional if MS/MSD performed)	One per matrix per prep batch of 20 or fewer samples upon request	</= 20 RPD </= 10 RPD for Drinking Waters	None
	MS/MSD	One per matrix per prep batch	+/- 25% of known concentration +/- 15% for Drinking Waters	None unless both spike recoveries very low, then PDS
	Post Digestion Spike (PDS)	When both MS and MSD recoveries are very low	+/- 15% of known concentration	None
	Continuing calibration verification (CCV)	After every 10 readings and at the end of the analysis sequence	+/- 10% of known concentration	Correct problem then re-read the CCV, CCB and all samples since last successful CCV/CCB; may report non-detects if CCV is biased high
	Continuing Calibration Blank (CCB)	After every CCV	+/- RL	Correct problem then re-read the CCV, CCB and all samples since last successful CCV/CCB; may report non-detects and results >10X the contamination level.
	MDL verification	Minimum yearly	Detectible	Re-evaluate standard used and MDL

Appendix 4: Summary of Calibration and QC Procedures for Mercury

Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
EPA245.1	Calibration curve – minimum 5 standards and blank	Quarterly, monthly, or daily – see individual SOP	r ≥ 0.995	Recalibrate
	Initial Calibration Verification – mid-level, second-source required (ICV)	Immediately following initial calibration and daily at the beginning of each analytical sequence.	±5% of known conc. (245.1)	Correct problem then repeat initial calibration; may report non-detects if biased high.
	Initial Calibration Blank (ICB)	After ICV	+/- RL	Correct problem then proceed; may report results >10X contamination level or non-detects if biased high
	CRA	One per calibration	No established limits	None
	Method blank	One per batch of 20 or fewer samples	+/- RL < ½ RL per QAPP	Correct problem then re-prep and analyze method blank and all samples processed with the contaminated blank. may report results >10X contamination level or non-detects if biased high
	LCS	One per batch of 20 or fewer samples	+/- 15% of known concentration	Correct problem, re-prep and repeat LCS, MB and all samples in the batch; may report non-detects if the LCS is biased high.
	Matrix duplicate	One per matrix per batch of 20 or fewer samples as requested	</= 20 RPD	Repeat once
	MS/MSD	One pair per matrix per batch of 20 or fewer samples	+/- 30% of known concentration	None
	Continuing calibration verification (CCV)	Beginning, every 10 samples, and at end of sequence	±10% of known concentration	Correct problem then repeat CCV, CCB and all samples since last successful CCB; may report non-detects if biased high.
	Continuing Calibration Blank (CCB)	After every CCV	+/- RL	Correct problem then repeat CCV,CCB and all samples since last successful CCB; may report results >10X contamination level or non-detects if biased high
	MDL verification	Minimum yearly	Detectible	Re-evaluate MDL standard used and MDL

Appendix 4: Summary of Calibration and QC Procedures for ICP Method 200.7

Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
EPA200.7	Initial calibration (three standards for each element- and a blank)	Daily initial calibration prior to sample analysis.	>/= 0.995	Re-calibrate
	Curve high-standards read-back	Daily after curve	+/- 5% of known concentration	Re-calibrate, re-run samples for affected elements
	Second-source calibration verification (ICV)	Daily after initial calibration	All analytes within 5% of expected value	Correct problem then repeat initial calibration; may report non-detects if biased high.
	Initial Calibration blank (ICB)	After ICV	+/- RL	Correct problem then re-analyze for affected elements; may report results >10X contamination level or non-detects if biased high
	CRI (2X RL)	At the beginning of an analytical run	50-150%	NA
	Interference check solution (ICSA)	At the beginning of an analytical run	+/- 20% of expected value of spiked elements or < 2X RL	Correct problem; re-analyze ICSA; re-analyze all affected samples; may report non-detects if biased high.
	Interference check solution (ICSB)	At the beginning of an analytical run	+/- 20% of expected value of spiked elements or < 2X RL	Correct problem; re-analyze ICSB; re-analyze all affected samples; may report non-detects if biased high.
	Method Blank	One per prep batch of </= 20 samples	+/- RL < ½ RL per QAPP	Correct problem, re-prep and re-analyze the method blank and all samples for affected elements; may report results >10X contamination level or non-detects if biased high
	LCS	One per prep batch of </= 20 samples	+/- 15% of known concentration	Correct problem, then re-prep and analyze the LCS and all samples for affected elements; may report non-detects if biased high.
	Method duplicate	One per 10 or fewer samples per matrix	</= 20 RPD	Repeat
	MS	One per 10 or fewer samples per matrix	+/- 30% of known concentration	None
	Dilution test	One per 10 or fewer samples per matrix	5x dilution must agree within 10% of the original determination	Perform post digestion spike addition
	Post Digestion Spike (PDS)	Performed when Dilution test fails	+/- 15% of known concentration	Narrate
	Continuing Calibration Verification (CCV)	After every 10 readings and at the end of the analytical sequence	All analytes within 10% of expected value	Correct problem and re-analyze affected elements of bracketed samples; may report non-detects if biased high.
	Continuing Calibration blank (CCB)	After each CCV	+/- RL	Correct problem and re-analyze affected elements of bracketed samples; may report results >10X contamination level or non-detects if biased high
	MDL verification	Minimum yearly	Detectible	Re-evaluate standard used and MDL

Appendix 4: Summary of Calibration and QC Procedures for ICP/MS Method 200.8

Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
EPA200.8	Initial calibration (one to three standards for each element- and a blank)	Daily initial calibration prior to sample analysis.	>/= 0.995	Re-calibrate
	Curve high-standards read-back	Daily after curve	+/- 5% of known concentration	Re-calibrate, re-run samples for affected elements
	Second-source calibration verification (ICV)	Daily after initial calibration	All analytes within 10% of expected value	Correct problem then repeat initial calibration; may report non-detects if biased high.
	Initial Calibration blank (ICB)	After ICV	+/- RL	Correct problem then re-analyze for affected elements; may report results >10X contamination level or non-detects if biased high
	CRI (2X RL)	At the beginning of an analytical run and every 12 hours	50-150%	NA
	Interference check solution (ICSA)	At the beginning of an analytical run and every 12 hours	+/- 20% of expected value of spiked elements or < 2X RL	Correct problem; re-analyze ICSA; re-analyze all affected samples; may report non-detects if biased high.
	Interference check solution (ICSB)	At the beginning of an analytical run and every 12 hours	+/- 20% of expected value of spiked elements or < 2X RL	Correct problem; re-analyze ICSB; re-analyze all affected samples; may report non-detects if biased high.
	Method Blank	One per prep batch of </= 20 samples	+/- RL < ½ RL per QAPP	Correct problem, re-prep and re-analyze the method blank and all samples for affected elements; may report results >10X contamination level or non-detects if biased high
	LCS	One per prep batch of </= 20 samples	+/- 15% of known concentration	Correct problem, then re-prep and analyze the LCS and all samples for affected elements; may report non-detects if biased high.
	Method duplicate	One per 10 or fewer samples per matrix	</= 20 RPD	Repeat
	MS	One per10 or fewer samples per matrix	+/- 30% of known concentration	None
	Dilution test	Each new sample matrix	5x dilution must agree within 10% of the original determination	Perform post digestion spike addition
	Continuing Calibration Verification (CCV)	After every 10 readings and at the end of the analytical sequence	All analytes within 10% of expected value	Correct problem and re-analyze affected elements of bracketed samples; may report non-detects if biased high.
	Continuing Calibration blank (CCB)	After each CCV	+/- RL	Correct problem and re-analyze affected elements of bracketed samples; may report results >10X contamination level or non-detects if biased high
	MDL verification	Minimum yearly	Detectible	Re-evaluate standard used and MDL

Appendix 4: Summary of Calibration and QC Procedures for Gravimetric Analyses

Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SM2540 C (TDS) SM2540D (TSS) SM2540B (TS) EPA160.4 SM2540E (TVS) ASTM D482-87 (Ash) ASTM D2974 (FOC) SM2540 G (Moisture) ASTM D5057 (Density)	LCS (applicable methods only: TDS; TSS; TS)	Applicable to some gravimetric testing - one per batch of 20 or fewer samples	+/- 20% of known concentration	Repeat LCS, MB and all samples in batch; May report non-detects if LCS is biased high.
	Method blank (if applicable – except for ASTM D5057)	One per batch of 20 or fewer samples	+/- RL < ½ RL per QAPP	Repeat MB, LCS and all samples in batch; May report non-detects and samples > 10X the contamination level.
	Duplicate (optional if MS/MSD performed)	10% of samples	</=20 RPD	None
	MS/MSD	Applicable to some gravimetric testing - one pair per set of 20 or fewer samples (except for ASTM D5057 and 160.4)	+/- 25% of known concentration	None
	MDL verification (applicable methods only: TDS; TSS; TS)	Minimum yearly	Detectible	Re-evaluate standard used and MDL

Appendix 4: Summary of Calibration and QC Procedures for Titrimetric Analyses

Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SM2320B Alkalinity forms SM4500 S2F SW9034/9030B Sulfide SM5220C COD SM4500Cl_F Cl_2 Res.	LCS	One per batch of 20 or fewer samples	± 20% of known concentration ± 15% SM2320B	Correct problem and repeat LCS, MB and all samples in the batch; May report non-detects if the LCS is biased high.
	Method blank	One per batch of 20 or fewer samples	No analyte detected > report limit	Correct problem and repeat MB, LCS and all samples in the batch; May report non-detects and samples >10X the contamination level
	Duplicate (optional if MS/MSD performed; Not performed for Sulfide)	One per batch of 20 or fewer samples	±20%	None
	MS/MSD (Not performed for SM2320B; SM4500Cl_F)	Available for some titrimetric tests at one pair per batch of 20 or fewer samples.	+/- 25% of known concentration	None
	Standardization	Per specific SOP	NA	NA
	MDL verification	Minimum yearly	Detectible	Re-evaluate standard used and MDL

Appendix 4: Summary of Calibration and QC Procedures for Spectrophotometric Analyses

Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
EPA 350.1* SM4500NH3G; NH_3. SM4500ClE*: 9251 Cl^-. SM3500CrB* 7196A Cr+6. SM4500SO4E SW9038: SO_4^{-2}. SM5310C 9060A: TOC. $SM4500NO_2B$ Nitrite EPA 353.2* $SM4500NO_3F$ NO7-0003 Nitrate-Nitrite 9066* EPA 420.4* Phenols SM4500P-E Phosphorus EPA 351.1 SM4500NH3G TKN	Calibration curve – minimum 5 standards and blank	Quarterly or daily – see individual SOP	r ≥ 0.995 y-intercept < abs. value of RL	Recalibrate
	Initial Calibration Verification – mid-level, second-source required (ICV)	Immediately following initial calibration and daily at the beginning of each analytical sequence.	±10% of known concentration	Correct problem then repeat initial calibration; may report non-detects if biased high.
	Initial Calibration Blank (ICB)	After ICV	+/- RL	Correct problem then proceed; may report results >10X contamination level or non-detects if biased high
	Nitrite Column Efficiency Standard (N3N2 analysis)	Daily after ICAL	90 -110%	Correct problem, repeat ICAL
	Method blank	One per batch of 20 or fewer samples One per 10 samples for 9066; 420.4	+/- RL < ½ RL per QAPP	Correct problem then re-prep and analyze method blank and all samples processed with the contaminated blank. may report results >10X contamination level or non-detects if biased high
	LCS	One per batch of 20 or fewer samples One per 10 samples for 9066; 420.4	+/- 20% of known concentration +/- 10% for * methods +/- 15% for Chloride methods	Correct problem, re-prep and repeat LCS, MB and all samples in the batch; may report non-detects if the LCS is biased high.
	Matrix duplicate (optional if MS/MSD performed)	One per matrix per batch of 20 or fewer samples as requested	</= 20 RPD </+ 10 RPD for * methods </= 30 RPD for soils	Repeat once
	MS/MSD	One pair per matrix per batch of 20 or fewer samples One per 10 samples for 353.2; 9060A; SM5310C; 9251	+/- 25% of known concentration +/- 10% for * methods	None
	Continuing calibration verification (CCV)	Beginning, every 10 samples, and at end of sequence	±10% of known concentration	Correct problem then repeat CCV, CCB and all samples since last successful CCB; may report non-detects if biased high.
	Continuing Calibration Blank (CCB)	After every CCV	+/- RL	Correct problem then repeat CCV,CCB and all samples since last successful CCB; may report results >10X contamination level or non-detects if biased high
	MDL verification	Minimum yearly	Detectible	Re-evaluate standard used and MDL

Appendix 4: Summary of Calibration and QC Procedures for Electrometric Analyses

Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SM5210B; BOD; CBOD; EPA120.1: SM2510B; SW9050A: Conductivity SM4500OG DO. SM4500FC; F- SM4500H+B SW9040B/C, SW9045C/D: pH.	Calibration Curve – minimum of 6 standards and blank (Fluoride only)	Initial Calibration before each batch (where applicable)	R ≥ 0.995.	Recalibrate
	Conductivity meter is calibrated with single standard in range of use.	Daily	Conductivity meter is adjusted to match known standard.	Correct problem then re-calibrate.
	pH Meter is calibrated using 3 pH Buffers	Daily	Must meet Slope requirements and pH buffer readback +/- 0.1 SU	Correct problem then re-calibrate.
	DO Meter is calibrated using water saturated air	Daily		Correct problem then re-calibrate
	Initial Calibration Verification (2nd source) (ICV-Fluoride only)	Immediately after initial calibration and daily at beginning of analytical sequence (where applicable)	±10% of known concentration	Correct problem then repeat initial calibration; may report non-detects if biased high.
	Initial Calibration Blank (ICB-Fluoride only)	With ICV (where applicable)	+/- RL	Correct problem then proceed; may report results >10X contamination level or non-detects if biased high
	Method blank (N/A for pH; Conductivity; DO)	One per batch of 20 or fewer samples (where applicable)	+/- RL < ½ RL per QAPP	Correct problem then re-prep and analyze method blank and all samples processed with the contaminated blank; may report results >10X contamination level or non-detects if biased high.
	LCS (N/A for Conductivity; DO)	One per batch of 20 or fewer samples (where applicable)	±20% of known concentration	Correct problem, re-prep and repeat LCS, MB and all samples in the batch; may report non-detects if the LCS is biased high.
	MS/MSD	Each batch (where applicable)	± 20%	None
	Duplicate	When spike not available	±20%	None
	Continuing Calibration verification (CCV) (N/A for BOD/CBOD; DO)	Beginning, every 10 samples, and end of batch (where applicable)	±10% of known concentration	Correct problem then repeat CCV, CCB and all samples since last successful CCB; may report non-detects if biased high.
	Continuing Calibration blank (N/A for BOD/CBOD; DO; Conductivity; pH)	With each CCV (where applicable)	+/- RL	Correct problem then repeat CCV,CCB and all samples since last successful CCB; may report results >10X contamination level or non-detects if biased high
	Calibration checks	Alternate pH buffers every 10 readings. Read-back DO calibration bottle. Conductivity standards must bracket samples in each range.	pH buffers +/- 0.2 SU DO bottle +/- 0.5 mg/L Cond. stds. After samples, <10% drift	Re-calibrate and re-read samples since last in-control check.
	MDL verification	Minimum yearly	Detectible	Re-evaluate standard used and MDL

Appendix 4: Summary of Calibration and QC Procedures for Ion Chromatographic Analyses

Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
EPA300; SW9056A Bromide Chloride Fluoride Nitrate Nitrite Sulfate O-Phosphate EPA 218.6 SW7199 CR+6	Calibration Curves	Initial calibration. Perform instrument re-calibration once per month minimum.	R ≥ 0.995.	Recalibrate
	Initial Calibration verification (ICV), second source	Immediately following initial calibration and daily before the analytical sequence	+/- 10% of known concentration +/- 5% for 218.6	Correct problem then repeat initial calibration; may report non-detects if biased high.
	Initial Calibration Blank	After ICV	+/- RL	Correct problem then proceed; may report results >10X contamination level or non-detects if biased high
	Method blank	One per batch of 20 or fewer samples	+/- RL < ½ RL per QAPP	Correct problem then re-prep and analyze method blank and all samples processed with the contaminated blank; may report results >10X contamination level or non-detects if biased high.
	LCS	One per batch of 20 or fewer samples	+/-10% of known concentration for 300.0, 218.6; 7199 +/- 20% for 9056	Correct problem, re-prep and repeat LCS, MB and all samples in the batch; may report non-detects if the LCS is biased high.
	MS/MSD	One pair per batch of 20 or fewer samples (9056A) One pair per batch of 10 or fewer samples (300.0)	+/- 20% of known concentration +/- 10% for 218.6; 7199	None, control batch on LCS
	Duplicate	One per batch of 20 or fewer samples upon request Note: Not required for 218.6; 7199	</= 20 RPD (300.0) </= 15 RPD (9056A)	None
	Continuing calibration verification (CCV)	After every 10 readings and at the end of the analytical sequence	+/- 10% of known concentration +/- 5% for 218.6	Correct problem then repeat CCV, CCB and all samples since last successful CCB; may report non-detects if biased high.
	Continuing Calibration blank (CCB)	After every CCV	+/- RL	Correct problem then repeat CCV,CCB and all samples since last successful CCB; may report results >10X contamination level or non-detects if biased high
	Retention time window	Based on RTs of ICV anions	+/- 5% drift	Evaluate data
	MDL verification	Minimum yearly	Detectible	Re-evaluate standard used and MDL

Appendix 4: Summary of Calibration and QC Procedures for Oil & Grease Analyses

Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
9071B 1664A 1664B HEM SGT-HEM	Method blank	One per batch of 20 or fewer samples	+/- RL < ½ RL per QAPP	Correct problem then re-prep and analyze method blank and all samples processed with the contaminated blank; may report results >10X contamination level or non-detects if biased high.
	LCS	One per batch of 20 or fewer samples	1664A, 1664B 78-114% for HEM, 64-132% for SGT-HEM 9071B 80 – 120% for HEM & SGT-HEM	Correct problem, re-prep and repeat LCS, MB and all samples in the batch; may report non-detects if the LCS is biased high.
	MS/MSD	Water: One MS per batch of 20 or fewer samples as available. Soils: One MS/MSD pair per batch of 20 or fewer samples (Note:additional sample bottles need to be submitted by the client for water samples for MS/MSD analysis)	1664A, 1664B 78-114% for HEM, 64-132% for SGT-HEM 9071B 75 – 125% for HEM & SGT-HEM	None, use LCS
	MDL verification	Minimum yearly	Detectible	Re-evaluate standard used and MDL

Appendix 4: Summary of Calibration and QC Procedures for Physical Analyses

Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SW1010B D-92: Flash Point.	STD - n-Decane (Flashpoint)	One per batch of 20 or fewer samples – applicable for flash point only	Method limit	Re-analyze
SW9095A: Paint Filter.	Duplicate	One for each batch of 20 or fewer samples Note: (Duplicates are not performed for Flashpoint or Paint Filter when samples are non-detect)	Report results	None

Appendix 5. Terms/Glossary and Acronyms (EL-V1M2 Sec. 3.1)

Acceptance Criteria:
Specified limits placed on characteristics of an item, process, or service defined in requirement documents. (ASQC)
Accreditation:
The process by which an agency or organization evaluates and recognizes a laboratory as meeting certain predetermined qualifications or standards, thereby accrediting the laboratory.
Accuracy:
The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator. (QAMS)
Analyst:
The designated individual who performs the "hands-on" analytical methods and associated techniques and who is the one responsible for applying required laboratory practices and other pertinent quality controls to meet the required level of quality.
Analytical Uncertainty:
A subset of Measurement Uncertainty that includes all laboratory activities performed as part of the analysis. (TNI)
Anomaly: A condition or event, other than a deficiency, that may affect the quality of the data, whether in the laboratory's control or not.
Assessment:
The evaluation process used to measure or establish the performance, effectiveness, and conformance of an organization and/or its systems to defined criteria (to the standards and requirements of laboratory accreditation). (TNI)
Audit:
A systematic and independent examination of facilities, equipment, personnel, training, procedures, record-keeping, data validation, data management, and reporting aspects of a system to determine whether QA/QC and technical activities are being conducted as planned and whether these activities will effectively achieve quality objectives. (TNI)
Batch:
Environmental samples which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples. (TNI)
Bias:
The systematic or persistent distortion of a measurement process, which causes errors in one direction (i.e., the expected sample measurement is different from the sample's true value). (TNI)
Blank:
A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results. (ASQC)
Calibration:
A set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material, and the corresponding values realized by standards. (TNI)

1) In calibration of support equipment the values realized by standards are established through the use of reference standards that are traceable to the International System of Units (SI).

2) In calibration according to methods, the values realized by standards are typically established through the use of Reference Materials that are either purchased by the laboratory with a certificate of analysis or purity, or prepared by the laboratory using support equipment that has been calibrated or verified to meet specifications.

Calibration Curve:
The mathematical relationship between the known values, such as concentrations, of a series of calibration standards and their instrument response. (TNI)

Calibration Standard:
A substance or reference material used to calibrate an instrument (QAMS)
Certified Reference Material (CRM):
A reference material accompanied by a certificate, having a value, measurement uncertainty, and stated metrological traceability chain to a national metrology institute. (TNI)
Chain of Custody (COC) Form:
Record that documents the possession of the samples from the time of collection to receipt in the laboratory. This record generally includes: the number and types of containers; the mode of collection; the collector; time of collection; preservation; and requested analyses. (TNI)
Compromised Samples:
Those samples which are improperly sampled, insufficiently documented (chain of custody and other sample records and/or labels), improperly preserved, collected in improper containers, or exceeding holding times when delivered to a laboratory. Under normal conditions, compromised samples are not analyzed. If emergency situation require analysis, the results must be appropriately qualified.
Confidential Business Information (CBI):
Information that an organization designates as having the potential of providing a competitor with inappropriate insight into its management, operation or products. TNI and its representatives agree to safeguarding identified CBI and to maintain all information identified as such in full confidentiality.
Confirmation:
Verification of the identity of a component through the use of an approach with a different scientific principle from the original method. These may include, but are not limited to: Second Column Confirmation; Alternate wavelength; Derivatization; Mass spectral interpretation; Alternative detectors or Additional Cleanup procedures. (TNI)
Conformance:
An affirmative indication or judgement that a product or service has met the requirements of the relevant specifications, contract, or regulation; also the state of meeting the requirements. (ANSI/ASQC E4-1994)
Correction:
Actions necessary to correct or repair analysis specific non-conformances. The acceptance criteria for method specific QC and protocols as well as the associated corrective actions. The analyst will most frequently be the one to identify the need for this action as a result of calibration checks and QC sample analysis. No significant action is taken to change behavior, process or procedure.
Corrective Action:
The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence. (ISO 8402)
Data Integrity: The condition that exists when data are sound, correct, and complete, and accurately reflect activities and requirements (TNI)
Data Audit:
A qualitative and quantitative evaluation of the documentation and procedures associated with environmental measurements to verify that the resulting data re of acceptable quality (i.e., that they meet specified acceptance criteria).
Data Reduction:
The process of transforming the number of data items by arithmetic or statistical calculations, standard curves, and concentration factors and collation into a more useable form. (TNI)
Deficiency:
An unauthorized deviation from acceptable procedures or practices, or a defect in an item. (ASQC)
Demonstration of Capability (DOC):
A procedure to establish the ability of the analyst to generate analytical results of acceptable accuracy and precision. (TNI)
Document Control:
The act of ensuring that documents (and revisions thereto) are proposed, reviewed for accuracy, approved for release by authorized personnel, distributed properly, and controlled to ensure use of the correct version at the location where the prescribed activity if performed. (ASQC)
Duplicate Analyses:
The analyses or measurements of the variable of interest performed identically on two subsamples of the same sample. The results from duplicate analyses are used to evaluate analytical or measurement precision but not the precision of sampling, preservation or storage internal to the laboratory. (EPA-QAD)
Equipment Blank:
Sample of analyte-free media which has been used to rinse common sampling equipment to check effectiveness of decontamination procedures.

External Standard Calibration:
Calibrations for methods that do not utilize internal standards to compensate for changes in instrument conditions.

Extraction Blank (LB, LB2, LB3):
A blank that has been taken through the extraction procedure such as TCLP/SPLP, 5035.

Field Blank:
Blank prepared in the field by filing a clean container with pure de-ionized water and appropriate preservative, if any, for the specific sampling activity being undertaken (EPA OSWER)

Field Duplicate:
Duplicate field-collected sample.

Field of Accreditation:
Those matrix, technology/method, and analyte combinations for which the accreditation body offers accreditation.

Good Laboratory Practices (GLP):
Formal regulations for performing basic laboratory operations outlined in 40 CFR Part 160 and 40 CFR Part 729 and required for activities performed under FIFRA and TSCA.

Holding Times:
The maximum times that samples may be held prior to analyses and still be considered valid or not compromised. (40 CFR Part 136)

Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical test method. (TNI)

Internal Standard Calibration: Calibrations for methods that utilize internal standards to compensate for changes in instrument conditions.

Internal Chain of Custody:
An unbroken trail of accountability that ensures the physical security of samples, data and records. Internal COC refers to additional documentation procedures implemented within the laboratory that includes special sample storage requirements, and documentation of all signatures and/or initials, dates, and times of personnel handling specific samples or sample aliquots.

Instrument Blank:
A clean sample (e.g., distilled water) processed through the instrumental steps of the measurement process; used to determine instrument contamination. (EPA-QAD)

Instrument Detection Limit (IDL):
The minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific instrument. The IDL is associated with the instrumental portion of a specific method only, and sample preparation steps are not considered in its derivation. The IDL is a statistical estimation at a specified confidence interval of the concentration at which the relative uncertainty is ± 100%. The IDL represents a range where qualitative detection occurs on a specific instrument. Quantitative results are not produced in this range.

Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample):
A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes, taken through all preparation and analysis steps of the procedure unless otherwise noted in a reference method. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.
An LCS shall be prepared at a minimum of 1 per batch of 20 or less samples per matrix type per sample extraction or preparation method except for analytes for which spiking solutions are not available such as total suspended solids, total dissolved solids, total volatile solids, total solids, pH, color, odor, temperature, dissolved oxygen or turbidity. The results of these samples shall be used to determine batch acceptance.

Least Squares Regression (1st Order Curve):
The least squares regression is a mathematical calculation of a straight line over two axes. The y axis represents the instrument response (or Response ratio) of a standard or sample and the x axis represents the concentration. The regression calculation will generate a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.99 for organics and 0.995 for inorganics.

Limit(s) of Detection (LOD) [a.k.a., Method Detection Limit (MDL)]:
The MDL is the minimum measured quantity of a substance that can be reported with 99% confidence that the concentration is distinguishable from method blank results, consistent with 40CFR Part 136 Appendix B, August, 2017.
LOD Verification [a.k.a., MDL Verification]:
A processed QC sample in the matrix of interest, spiked with the analyte at no more than 3X the LOD for single analyte tests and 4X the LOD for multiple analyte tests and processed through the entire analytical procedure.
Limit(s) of Quantitation (LOQ) [a.k.a., Reporting Limit]:
The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence. The LOQ shall be set at or above the concentration of the lowest calibration standard. The laboratory's routine reporting limit is equal to the LOQ, unless project documents specifies a higher concentration to be used as the project-specific reporting limit.
Matrix (QS):
The component or substrate that contains the analyte of interest. For purposes of batch and QC requirement determinations, the following matrix distinctions shall be used:

- Aqueous: Any aqueous sample excluded from the definition of Drinking Water matrix or Saline/Estuarine source. Includes surface water, groundwater, effluents, and TCLP or other extracts.
- Drinking Water: any aqueous sample that has been designated as a potable or potential potable water source.
- Saline/Estuarine: any aqueous sample from an ocean or estuary, or other salt water source such as the Great Salt Lake.
- Non-aqueous Liquid: any organic liquid with <15% settleable solids.
- Biological Tissue: any sample of a biological origin such as fish tissue, shellfish, or plant material. Such samples shall be grouped according to origin.
- Solids: includes soils, sediments, sludges, and other matrices with ≥15% settleable solids.
- Chemical Waste: a product or by-product of an industrial process that results in a matrix not previously defined.
- Air & Emissions: Whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas or vapor that are collected with a sorbant tube, impinger solution, filter, or other device. (TNI)

Matrix Spike (spiked sample or fortified sample):
A sample prepared, taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a referenced method, by adding a known amount of target analyte to a specified amount of sample for which an independent test result of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.
Matrix Spike Duplicate (spiked sample or fortified sample duplicate):
A replicate matrix spike is prepared and analyzed to obtain a measure of the precision of the recovery for each analyte.
Method Blank:
A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.
Method Detection Limit:
See Limit of Detection (LOD)
Method Detection Limit Check Standard (MDLCK/MDLV):
A standard that is processed with the MDL Study that is spiked at ½ the spike level used for the MDL/DL study or ½ the method reporting limit or ½ the lowest calibration standard (RL/LOQ). This check standard is also referred to as the MDLV.
Method Reporting Limit Check Standard (MRL):
A standard that is not processed with the samples. It is analyzed in the analytical sequence at a spike concentration approximately 2x the low standard or reporting limit.
Negative Control:
Measures taken to ensure that a test, its components, or the environment do not cause undesired effects, or produce incorrect test results.

Non-conformance:
An indication, judgment, or state of not having met the requirements of the relevant specifications, contract, or regulation.
Non-conformance Memo (NCM):
The term for the mechanism used in the TALs LIMs to document a non-conformance to a job, project, program or method analysis in the system.
Observation: A record of phenomena that (1) may assist in evaluation of the sample data; (2) may be of importance to the project manager and/or the client, and yet not at the time of the observation have any known effect on quality.
Performance Audit:
The routine comparison of independently obtained qualitative and quantitative measurement system data with routinely obtained data in order to evaluate the proficiency of an analyst or laboratory.
Positive Control:
Measures taken to ensure that a test and/or its components are working properly and producing correct or expected results from positive test subjects.
Precision:
The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms. (TNI)
Preservation:
Any conditions under which a sample must be kept in order to maintain chemical and/or biological integrity prior to analysis. (TNI)
Proficiency Testing:
A means of evaluating a laboratory's performance under controlled conditions relative to a given set of criteria through analysis of unknown samples provided by an external source. (TNI)
Proficiency Testing Program:
The aggregate of providing rigorously controlled and standardized environmental samples to a laboratory for analysis, reporting of results, statistical evaluation of the results and the collective demographics and results summary of all participating laboratories. (TNI)
Proficiency Test Sample (PT):
A sample, the composition of which is unknown to the laboratory and is provided to test whether the analyst/laboratory can produce analytical results within specified acceptance criteria. (TNI)
Proprietary:
Belonging to a private person or company.
Quality Assurance:
An integrated system of management activities involving planning, implementation, assessment, reporting and quality improvement to ensure that a process, item, or service is of the type of quality needed and expected by the client. (TNI)
Quality Assurance [Project] Plan (QAPP):
A formal document describing the detailed quality control procedures by which the quality requirements defined for the data and decisions pertaining to a specific project are to be achieved. (EAP-QAD)
Quality Control:
The overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer; operational techniques and activities that are used to fulfill requirements for quality; also the system of activities and checks used to ensure that measurement systems are maintained within prescribed limits, providing protection against "out of control" conditions and ensuring that the results are of acceptable quality. (TNI)
Quality Control Sample:
A sample used to assess the performance of all or a portion of the measurement system. One of any number of samples, such as Certified Reference Materials, a quality system matrix fortified by spiking, or actual samples fortified by spiking, intended to demonstrate that a measurement system or activity is in control. (TNI)
Quality Manual:
A document stating the management policies, objectives, principles, organizational structure and authority, responsibilities, accountability, and implementation of an agency, organization, or laboratory, to ensure the quality of its product and the utility of its product to its users. (TNI)

Quality System:
A structured and documented management system describing the policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for ensuring quality in its work processes, products (items), and services. The quality system provides the framework for planning, implementing, and assessing work performed by the organization and for carrying out required QA and QC activities. (TNI)

Raw Data:
The documentation generated during sampling and analysis. This documentation includes, but is not limited to, field notes, electronic data, magnetic tapes, untabulated sample results, QC sample results, print outs of chromatograms, instrument outputs, and handwritten records. (TNI)

Record Retention:
The systematic collection, indexing and storing of documented information under secure conditions.

Reference Material:
Material or substance one or more properties of which are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials. (TNI)

Reference Standard:
Standard used for the calibration of working measurement standards in a given organization or a given location. (TNI)

Replicate Analyses:
The measurements of the variable of interest performed identically on two or more sub-samples of the same sample within a short time interval.

Sampling:
Activity related to obtaining a representative sample of the object of conformity assessment, according to a procedure.

Sampling and Analysis Plan (SAP):
A formal document describing the detailed sampling and analysis procedures for a specific project.

Second Order Polynomial Curve (Quadratic):
The 2nd order curves are a mathematical calculation of a slightly curved line over two axis. The y axis represents the instrument response (or Response ratio) of a standard or sample and the x axis represents the concentration. The 2nd order regression will generate a coefficient of determination (COD or r^2) that is a measure of the "goodness of fit" of the quadratic curvature the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r^2 must be greater than or equal to 0.99.

Selectivity:
The ability to analyze, distinguish, and determine a specific analyte or parameter from another component that may be a potential interferent or that may behave similarly to the target analyte or parameter within the measurement system. (TNI)

Sensitivity:
The capability of a method or instrument to discriminate between measurement responses representing different levels (e.g., concentrations) of a variable of interest. (TNI)

Spike:
A known mass of target analyte added to a blank, sample or sub-sample; used to determine recovery efficiency or for other quality control purposes.

Standard:
The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of standard setting and meets the approval requirements of standard adoption organizations procedures and policies. (TNI)

Standard Operating Procedures (SOPs):
A written document which details the method for an operation, analysis, or action, with thoroughly prescribed techniques and steps. SOPs are officially approved as the methods for performing certain routine or repetitive tasks. (TNI)

Storage Blank:
A blank matrix stored with field samples of a similar matrix (volatiles only) that measures storage contribution to any source of contamination.

Surrogate:
A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.
Surrogate compounds must be added to all samples, standards, and blanks, for all organic chromatography methods except when the matrix precludes its use or when a surrogate is not available. Poor surrogate recovery may indicate a problem with sample composition and shall be reported to the client whose sample produced poor recovery. (QAMS)
Systems Audit (also Technical Systems Audit):
A thorough, systematic, qualitative on-site assessment of the facilities, equipment, personnel, training, procedures, record keeping, data validation, data management, and reporting aspects of a total measurement system. (EPA-QAD)
Technical Manager:
A member of the staff of an environmental laboratory who exercises actual day-to-day supervision of laboratory operations for the appropriate fields of accreditation and reporting of results
Technology:
A specific arrangement of analytical instruments, detection systems, and/or preparation techniques.
Traceability:
The ability to trace the history, application, or location of an entity by means of recorded identifications. In a calibration sense, traceability relates measuring equipment to national or international standards, primary standards, basic physical constants or properties, or reference materials. In a data collection sense, it relates calculations and data generated throughout the project back to the requirements for the quality of the project. (TNI)
Trip Blank:
A blank matrix placed in a sealed container at the laboratory that is shipped, held unopened in the field, and returned to the laboratory in the shipping container with the field samples.
Uncertainty:
A parameter associated with the result of a measurement that characterizes the dispersion of the value that could reasonably be attributed to the measured value.

Acronyms:

CAR – Corrective Action Report	LIMS – Laboratory Information Management System
CCV – Continuing Calibration Verification	MDL – Method Detection Limit
CF – Calibration Factor	MDLCK – MDL Check Standard
CFR – Code of Federal Regulations	MDLV – MDL Verification Check Standard
COC – Chain of Custody	MRL – Method Reporting Limit Check Standard
DL – Detection Limit	MS – Matrix Spike
DLCK – Detection Limit Check Standard	MSD – Matrix Spike Duplicate
DOC – Demonstration of Capability	NCM – Non-Conformance Memo
DQO – Data Quality Objectives	NELAP - National Environmental Laboratory Accreditation Program
DUP - Duplicate	PT – Performance Testing
EHS – Environment, Health and Safety	TNI – The NELAC Institute
EPA – Environmental Protection Agency	QAM – Quality Assurance Manual
GC - Gas Chromatography	QA/QC – Quality Assurance / Quality Control
GC/MS - Gas Chromatography/Mass Spectrometry	QAPP – Quality Assurance Project Plan
ICP - Inductively Coupled Plasma Atomic Emission Spectroscopy	RF – Response Factor
ICP/MS – ICP/Mass Spectrometry	RPD – Relative Percent Difference
ICV – Initial Calibration Verification	RSD – Relative Standard Deviation
IDL – Instrument Detection Limit	SD – Serial Dilution
IH – Industrial Hygiene	SDS - Safety Data Sheet
IS – Internal Standard	SOP- Standard Operating Procedure
LCS – Laboratory Control Sample	TAT – Turn-Around-Time
LCSD – Laboratory Control Sample Duplicate	VOA – Volatiles
LOD – Limit of Detection	VOC – Volatile Organic Compound
LOQ – Limit of Quantitation	
LLOQ – Lower Limit of Quantitation	

Appendix 6.

Laboratory Certifications, Accreditations, Validations

Eurofins Chicago maintains accreditations, certifications, and approvals with numerous state and national entities. Programs vary but may include on-site audits, reciprocal agreements with another entity, performance testing evaluations, review of the QA Manual, Standard Operating Procedures, Method Detection Limits, training records, etc. At the time of this QA Manual revision, the laboratory has accreditation/certification/licensing with the following organizations:

Laboratory	Authority	Program	EPA Region	Certification ID
Eurofins Chicago	California	State Program	9	2903
Eurofins Chicago	Georgia	State Program	4	939
Eurofins Chicago	Georgia	State Program	4	N/A
Eurofins Chicago	Hawaii	State Program	9	N/A
Eurofins Chicago	Illinois	NELAP	5	IL00035
Eurofins Chicago	Indiana	State Program	5	C-IL-02
Eurofins Chicago	Iowa	State Program	7	082
Eurofins Chicago	Kansas	NELAP	7	E-10161
Eurofins Chicago	Kentucky (UST)	State Program	4	AI#108083
Eurofins Chicago	Kentucky (WW)	State Program	4	KY90023
Eurofins Chicago	Louisiana	NELAP	6	02046
Eurofins Chicago	Mississippi	State Program	4	N/A
Eurofins Chicago	North Carolina (WW/SW)	State Program	4	291
Eurofins Chicago	North Dakota	State Program	8	R-194
Eurofins Chicago	Oklahoma	State Program	6	8908
Eurofins Chicago	South Carolina	State Program	4	77001003
Eurofins Chicago	USDA	Federal		P330-15-00018
Eurofins Chicago	Wisconsin	State Program	5	999580010
Eurofins Chicago	Wyoming	State Program	8	8TMS-Q

Accreditation may not be offered or required for all methods and analytes reported in this package. Please contact your project manager for the laboratory's current list of certified methods and analytes.

The certificates and accredited parameter lists are available, for each State/Program at www.EurofinsUS.com/Env under Analytical Services Search - Certifications.

Appendix 7. Example: Data Qualifiers – Standard Flagging Suite

Flag	Flag Text
!	Laboratory is not accredited for this parameter
*	Recovery or RPD exceeds control limits (LCS, LCSD; MS; MSD; Surrogate; Serial Dilution)
*	ISTD response or retention time outside acceptable limits
*	ICPMS Relative Intensity is outside the method limits
+	MSA correlation coefficient is less than 0.995
<	The analyte is not detected at or above the indicated concentration
>	The analyte exceeded the indicated concentration
^	Instrument related QC is outside acceptance limits. (ICV, CCV, ICB, CCB, ISA, ISB, CRI, CRA, DLCK or MRL Standard)
4	MS, MSD: The analyte present in the original sample is greater than 4 times the matrix spike concentration; therefore, control limits are not applicable.
A	The tentatively identified compound is a suspected aldol-condensation product.
B	Compound was found in the blank and sample.
b	Result Detected in the Unseeded Control Blank (USB)
cn	Refer to Case Narrative for further detail
D	Sample results are obtained from a dilution; the surrogate or matrix spike recoveries reported are calculated from diluted samples.
D	Surrogate or matrix spike recoveries were not obtained because the extract was diluted for analysis; also compounds analyzed at a dilution may be flagged with a D.
DW	Result has been dry weight corrected
E	Result exceeded calibration range.
F1	MS and/or MSD Recovery is outside acceptance limits
F2	MS/MSD RPD exceeds the control limits
F3	Duplicate RPD exceeds the control limit
F5	Duplicate RPD exceeds limit, and one or both sample results are less than 5 times RL. The data are considered valid because the absolute difference is less than the RL.
H	Sample was prepped or analyzed beyond the specified holding time
H3	Sample was received and analyzed past holding time
HF	Field parameter with a holding time of 15 minutes. Test performed by laboratory at client's request.
I	Indicates the presence of an interference, recovery is not calculated.
J	Indicates an Estimated Value for TICs
J	Result is less than the RL but greater than or equal to the MDL and the concentration is an approximate value.
K	Benzo(b&k)fluoranthene are unresolved due to matrix, result is reported as Benzo(b)fluoranthene
L	A negative instrument reading had an absolute value greater than the reporting limit
NC	Not Confirmed
ND	Compound not detected
P	The %RPD between the primary and confirmation column/detector is >40%. The higher value has been reported.
p	The %RPD between the primary and confirmation column/detector is >40%. The lower value has been reported.
q	The reported result is the estimated maximum possible concentration of this analyte, quantitated using the theoretical ion ratio. The measured ion ratio does not meet the qualitative identification criteria and indicates a possible interference.

Flag	Flag Text
R	The instrument was not calibrated for this compound. A non-detect indicates that the characteristic ions were not present and the compound was not qualitatively identified. No controls were present to determine either sample preparation efficiency or the instrument sensitivity for the compound. As a result, the limit of detection is not known and the reported concentrations are estimates.
S	Result was determined by the Method of Standard Additions
s	SCB Recovery Exceeds Limits
S1	Surrogate recovery exceeds control limits
T	Identification of this analyte is supported by comparison of retention time and mass spectrum to that of a reference standard. Complete calibration has not been performed and values should be considered as estimated.
U	Indicates the analyte was analyzed for but not detected.
V	Serial Dilution exceeds the control limits
W	PS: Post-digestion spike was outside control limits
Y	The chromatographic response resembles a typical fuel pattern.
Z	The chromatographic response does not resemble a typical fuel pattern.

Appendix 8 Method Capability Listing

Unit	Parameter	Method No.	NELAP	Matrix
GCE	Pesticides/PCBs	EPA 608	X	W
GCE	Pesticides/PCBs	EPA 608.3	X	W
GCE	Organochlorine Pesticides	SW 8081A / 8081B	X	W/S
GCE	PCBs	SW 8082A	X	W/S
GCE	Chlorinated Herbicides by GC	SW 8151A	X	W/S
GCV	Petroleum Hydrocarbons (DRO)	SW 8015B / 8015C / 8015D	X	W/S
GCV	Petroleum Hydrocarbons (GRO)	SW 8015B / 8015C / 8015D	X	W/S
M	Hardness (Ca, Mg)	SM 2340B – 1997;2011	X	W
M	ICP Metals	EPA 200.7 - 1994	X	W
M	ICP-MS Metals	EPA 200.8 - 1994	X	W
M	CVAA Mercury	SW 7470A	X	W
M	CVAA Mercury	SW 7471B	X	S
M	CVAA Mercury	EPA245.1 R3.0 - 1994	X	W
M	ICP Metals	SW 6010B; 6010C	X	W/S
M	ICP Metals	SW 6010D	X	W/S
M	ICP-MS Metals	SW 6020	X	W
M	ICP-MS Metals	SW 6020A	X	W
M	ICP-MS Metals	SW 6020B	X	W
MSB	GC/MS Semi-Volatiles	EPA 625	X	W
MSB	GC/MS Semi-Volatiles	EPA 625.1	X	W
MSB	GC/MS Semi-Volatiles	SW 8270C / 8270D	X	W/S
MSB	GC/MS Semi-Volatiles	SW 8270E		W/S
MSB	GC/MS Semi-Volatiles	SW 8270C (SIM)		W
MSV	VOAs by GC/MS	EPA 624	X	W
MSV	VOAs by GC/MS	EPA 624.1	X	W
MSV	GC/MS Volatiles	SW 8260B	X	W/S
MSV	GC/MS Volatiles	SW 8260D		W/S
P	GC/MS Water VOAs	SW 5030B	X	W
P	GC/MS Soil VOAs in EnCore Samples	SW 5035 / 5035A		S
P	TCLP	SW 1311	X	W/S
P	SPLP	SW 1312	X	W/S
P	Extractable Organics; Separatory Funnel	SW 3510C		W
P	Extractable Organics; Accel. Soxhlet	SW 3541		S
P	Extractable Organics; Sonication	SW 3550B / 3550C		S
P	Acid Cleanup	SW 3665A		W/S
P	Alumina Cleanup	SW 3610B		W/S
P	Florisil Clean-up	SW 3620B		W/S
P	Silica Gel Clean-up	SW 3630C		W/S

Unit	Parameter	Method No.	NELAP	Matrix
P	Gel Permeation Column Clean-up	SW 3640A		S
P	Sulfur Clean-up	SW 3660B		W/S
P	Waste Dilution	SW 3580A		S
P	Metals Digestions; Surface/Ground Water for ICP / ICPMS	SW 3005A		W
P	Metals Digestions; Waters/Extracts for ICP	SW 3010A		W
P	Metals Digestions; Soils/Wastes for ICP / ICPMS	SW 3050B		S
W	Alkalinity	SM 2320B – 1997;2011	X	W/S
W	Ammonia	EPA 350.1 R2.0 – 1993	X	W/S
W	Ammonia	SM 4500NH3G – 1997;2011	X	W/S
W	BOD - 5 Day	SM 5210B – 2001;2011	X	W
W	Bromide, IC	EPA 300.0 R2.1 – 1993	X	W
W	Bromide, IC	SW-846 9056A	X	W/S
W	Carbonaceous BOD	SM 5210B – 2001; 2011	X	W
W	Chloride (AQ2-Seal)	SM 4500Cl E - 1997	X	W/S
W	Chloride (AQ2-Seal)	SW-846 9251	X	W/S
W	Chloride, IC	EPA 300.0 R2.1 - 1993	X	W
W	Chloride, IC	SW-846 9056A	X	W/S
W	Chlorine, Residual	SM 4500 Cl F – 2000;2011	X	W
W	Chlorine, Residual (Field)	SM 4500 Cl G – 2000;2011	X	W
W	COD - High Level	SM 5220C – 1997;2011	X	W/S
W	COD - Low Level	SM 5220C – 1997;2011	X	W/S
W	Chromium, Hexavalent	SM 3500-CrB – 2009;2011	X	W/S
W	Chromium, Hexavalent	SW-846 3060A/7196A	X	W/S
W	Chromium, Hexavalent	EPA 218.6 R3.3 – 1994	X	W
W	Chromium, Hexavalent	SW-846 7199	X	W
W	Cyanide, Total	SW-846 9012B	X	W/S
W	Cyanide, Amenable	SW-846 9012B		W/S
W	Cyanide, Total	EPA 335.4 Rev1	X	W
W	Cyanide, Amenable	EPA 335.4 Rev1		W
W	Ferrous Iron	SM 3500 Fe B		W/S
W	Flashpoint	SW-846 1010B		W
W	Fluoride	SM 4500F C – 1997’2011	X	W/S
W	Fluoride, IC	EPA 300.0 R2.1 – 1993	X	W
W	Fluoride, IC	SW-846 9056A	X	W/S
W	Nitrate-NO2 (AQ2)	EPA 353.2 R2.0 – 1993	X	W/S
W	Nitrate-NO2 (AQ2)	SM 4500NO3F – 2000;2011	X	W/S
W	Nitrate-NO2	NECi N07-0003	X	W/S
W	Nitrate, IC	EPA 300.0 R2.1 – 1993	X	W

Unit	Parameter	Method No.	NELAP	Matrix
W	Nitrate, IC	SW-846 9056A	X	W/S
W	Nitrite	SM 4500NO2B –2000;2011	X	W/S
W	Nitrite, IC	EPA 300.0 R2.1 - 1993	X	W
W	Nitrite, IC	SW-846 9056A	X	W/S
W	Oil & Grease (HEM; SGT-HEM)	EPA 1664A; EPA 1664B	X	W
W	Oil & Grease (HEM; SGT-HEM)	SW-846 9071B	X	S
W	Oxygen, Dissolved	SM 4500 O G – 2001;2011	X	W
W	pH - Low/High	SM 4500H+B – 2000;2011	X	W
W	pH - Low/High	SW-846 9045C / 9045D	X	S
W	pH - Low/High	SW-846 9040B / 9040C	X	W
W	Paint Filter	SW-846 9095A / 9095B	X	W
W	Phenol (AQ2)	EPA 420.4 R1.0 – 1993	X	W/S
W	Phenol (AQ2)	SW-846 9066	X	W/S
W	Phosphate, Ortho	SM 4500 PE – 1999;2011	X	W/S
W	Phosphate, Ortho , IC	EPA 300.0 R2.1 – 1993	X	W
W	Phosphate, Ortho , IC	SW-846 9056A	X	W/S
W	Phosphorus	SM 4500 P E – 1999;2011	X	W/S
W	Specific Conductance	EPA 120.1 – 1982	X	W
W	Specific Conductance	SM 2510B – 1997;2011	X	W
W	Specific Conductance	SW-846 9050A	X	W/S
W	Specific Gravity	SM 2710F		W/S
W	Sulfate - Turbidimetric	SW-846 9038M	X	W
W	Sulfate - Turbidimetric	SM 4500 SO4E –1997;2011	X	W
W	Sulfate, IC	EPA 300.0 R2.1 - 1993	X	W
W	Sulfate, IC	SW-846 9056A	X	W/S
W	Sulfide	SM 4500SF – 2000;2011	X	W/S
W	Sulfide	SW-846 9030B/9034	X	W/S
W	TKN	SM 4500 NH3G – 1997	X	W/S
W	TKN	EPA 351.1 – 1978	X	W/S
W	TOC/DOC (TIC/DIC) [Organic Carbon; Inorganic & Dissolved]	SM 5310C – 2000;2011	X	W
W	TOC/DOC (TIC/DIC) [Organic Carbon; Inorganic & Dissolved]	SW-846 9060A	X	W
W	TS - Water (Total Solids)	SM 2540B – 1997;2011	X	W
W	TS - Solid (Total Solids)	SM 2540G		S
W	TSS (Total Suspended Solids)	SM 2540D – 1997; 2011	X	W
W	TDS (Total Dissolved Solids)	SM 2540C – 1997;2011	X	W
W	Turbidity	EPA 180.1 R2.0 – 1993	X	W
W	TVS (Total Volatile Solids)	EPA 160.4 – 1971	X	W
W	TVS (Total Volatile Solids)	SM 2540E – 1997;2011	X	W
W	TVDS (Total Volatile Dissolved Solids)	EPA 160.4 – 1971	X	W

Unit	Parameter	Method No.	NELAP	Matrix
W	TVDS (Total Volatile Dissolved Solids)	SM 2540E – 1997;2011	X	W
W	TVSS (Total Volatile Suspended Solids)	EPA 160.4 – 1971	X	W
W	TVSS (Total Volatile Suspended Solids)	SM 2540E – 1997;2011	X	W

Matrix: W (Water) S (Soil/Solid)
Note: NELAP accreditation may be matrix and program specific. Refer to Eurofins Chicago's IL NELAP Accreditation Number: 100201

Appendix D

Laboratory Documentation: Standard Operating Procedures

TITLE: Metals Analysis
Trace Inductively Coupled Argon Plasma

Approvals (Signature/Date):

Debbie Johnson 8-2-23
Debbie Johnson — Date
Supervisor, Metals

Nicole Berg 8/4/23
Nicole Berg — Date
Quality Assurance Manager

8/2/23
Chris Hoham — Date
Env. Health & Safety Coor.

8/2/23
Ray Shock, III — Date
Technical Director

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1.0 SCOPE / APPLICATION

This procedure describes the analysis of trace elements including metals in solution by Inductively Coupled Plasma -Optical Emission Spectroscopy (ICP-OES) or Trace Inductively Coupled Argon Plasma (ICAP) Emission Spectrometry - Simultaneous Operation using SW-846 Method 6010B, 6010C, 6010D and EPA Method 200.7. The hardness calculations found in Section 9.4 are from Standard Methods, 2340 B-97 and 2340 B 23rd ED.

On occasion, clients request slight modifications to this SOP for non-drinking water samples. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP), authorized via laboratory signature approval, and mentioned in the data package's case narrative. **Note: There are no method modifications allowed for Drinking Water samples without prior written approval from US EPA.**

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants" with additional details are provided in the Eurofins Corporate SOP, *NDSC-QA-SOP42091, Detection and Quantitation Limits* and the Eurofins Chicago SOP, *UP-QA-017, Method Detection Limit Studies.* MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; the MDL Study will be performed and verified on an annual basis, verifying the Lower Limit of Quantitation (LLOQ) for the method.

1.1.2 Demonstration of Capability

Before the laboratory may institute a new method and begin reporting results, the laboratory shall confirm that it can properly operate the method. A demonstration of capability is performed whenever there is a change in instrument type, method or personnel. An Initial Demonstration of Capability (IDOC) must be thoroughly documented and approved by the Department Manager/Supervisor and QA Manager prior to independently analyzing client samples. All associated documentation must be retained in the QA Department and in the Analyst Training files. For additional details on the demonstration of capability procedures followed, refer to the laboratory SOP, *UP-QA-QAM, Quality Assurance Manual, Sections 19.4.2 and 19.4.3.*

1.1.3 Instrument Detection Limits

Instrument Detection Limits (IDLs) are performed on an annual basis for each element and for each instrument. The IDLs can be estimated as the mean of the blank results plus three times the standard deviation of 10 replicate analyses of the reagent blank solution. These limits are used to gauge both instrument sensitivity and instrument performance. Note: IDLs are also required after major maintenance such as changing the detector on the instrument.

1.1.4 Reporting Limits (LLOQ)

Reporting Limits (LLOQ) are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. The laboratory maintains reporting limits that are higher than the MDL. Wherever possible, reporting is limited to values ~3-5x the respective MDL to ensure confidence in the value reported. Client specific requests for reporting to the MDL are special circumstances not to be confused with the previous statement. Refer to Table 1 for element wavelengths and reporting limits.

1.1.5 Definitions

Refer to Section 3.0 of the Laboratory's Quality Assurance Manual (UP-QA-QAM).

1.2 Summary of Method

Inductively Coupled Plasma – Atomic Emission Spectrometer (ICP-AES, ICP-OES, ICP, or ICAP) is a technique for the analysis of water samples and aqueous solutions (including digested solids) for metals concentration using optical emission produced as the sample is introduced to argon plasma. The instruments are capable of simultaneous analysis of 29 different elements per sample.

All matrices, including water, TCLP extracts, wastes, soils, sludges and sediments, require digestion prior to analysis.

Only method 200.7 is applicable for drinking water analysis. Either method may be used for the determination of dissolved and total recoverable elements in ground waters, surface waters, wastewaters, leachates, and solids. Samples for method 200.7 dissolved metals and drinking waters with a turbidity of <1 NTU are analyzed without digestion. All other matrices, including water, TCLP extracts, wastes, soils, sludges and sediments, require digestion prior to analysis. The digestion methods are written in a separate SOP.

2.0 INTERFERENCES

Spectral, Physical and Chemical Interferences are the three main interferences that are commonly present on the ICAP.

2.1 Spectral Interferences

Spectral interferences are caused by background emission from continuous or recombinant phenomena, stray light from a high concentration element or overlap of a spectral line from another element. The instrument can correct for the first three types of interferences by using background correction adjacent to the wavelength. Spectral overlap can be corrected by using an alternate wavelength or monitoring the interfering wavelength and computer correcting the results for the false concentration using a predetermined ratio. The values used to correct are known as Inter-Element Correction Factors (IECs). See Section 6.1. Interferent Check Standard A (ICSA) is monitored to detect drift requiring the IEC equations to be corrected.

2.2 Physical Interferences

Physical interferences are usually associated with the sample uptake and nebulization processes. These interferences can usually be eliminated by using a peristaltic pump which ensures a

constant sample uptake rate. If a sample is extremely viscous or contains a very high dissolved solids concentration, a dilution of the sample may be required to ensure a constant and smooth nebulization rate. A high solids nebulizer, a mass flow controller and an argon humidifier are used prior to nebulization to minimize physical interferences. If internal standard counts indicate matrix interference a dilution on the sample will be performed.

2.3 Chemical Interferences

Chemical interferences are normally not significant on the ICAP. These interferences include ionization effects and molecular compound formation. Chemical interferences are highly dependent on the sample matrix type and the element.

Most of the interferences can be corrected by ensuring a constant sample uptake rate and by using the correcting abilities of the computer. If severe interferences are suspected, an alternate method such as ICPMS can be used or to verify the ICAP results.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual, Lab Specific Addendum to the CSM, and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coat and closed-toe, nonabsorbent shoes are a minimum.

3.1 Specific Safety Concerns or Requirements

- The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.
- Parts of the instrument can be extremely hot. Care should be taken if the instrument needs to be adjusted internally.
- Proper ventilation is required due to sample fumes and extreme heat generation (RF generator and plasma) and plasma emissions. People with medical conditions that may respond to ozone emissions should exercise caution.
- Individuals with pacemakers must be aware that the instrument radio frequency generator may interfere with pacemaker operation.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material[1]	Hazards	Exposure Limit[2]	Signs and Symptoms of Exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 EQUIPMENT AND SUPPLIES

Thermo Fisher ICAP 6500. This ICAP currently has 32 analytical wavelengths with additional wavelengths available. It is equipped with a peristaltic pump for sample uptake and an autosampler, and uses TJA iTEVA software. The ThermoFisher ICAP instruments use the following high solids nebulizer: Thermo Scientific C2 Aerosalt 35 PSI Concentric Nebulizer Argon and Sample Disconnect.

4.1 Supplies

- Volumetric Flasks (Class A): 100 mL, 200 mL, 500 mL, 1000 mL; 2000 mL
- Eppendorf Pipettes, varying volumes
- Low Range pH paper 0.0 to 3.0 S.U.
- Glass Expansion Rinse Attachment

5.0 REAGENTS AND STANDARDS

Note: All reagents and blank solutions prepared daily must include the following information on the container labels: date of preparation, method identification, reagent or blank identification, relevant SOP section.

All purchased reagents and standards require a peer review to be documented in TALS.

5.1 Reagents

- Milli-Q Water
- Concentrated Nitric Acid (HNO_3) - ACS Plus grade or better
- Concentrated Hydrochloric Acid (HCl) - ACS Plus grade or better
- Internal Standards: Ytrium (Y); Indium (In); Profile Standard Zinc(Zn)–CPI International

5.2 Stock Standards and QC Solutions

All stock standards and QC solutions are purchased from an outside supplier in aqueous form. The suppliers that are currently used are Inorganic Ventures, Hi Purity, CPI and Agilent. Two types of standards are used: single element and custom mixed standards. Single element standards are available for most elements at a 1,000 mg/L concentration. The shelf life of all purchased solutions are as stated by the manufacturer and are listed in TALS.

5.2.1 Internal Standards

The Thermo Fisher ICAP 6500 Duo uses Yttrium and Indium as internal Standards. Individual stock solutions are purchased to make up the solution.

Standard	Preparation
Internal standard	• Add 500 mL Milli-Q water to 1L Class A Volumetric Flask • Re-pipette 10 mL of HNO_3 into the flask • Re-pipette 50 mL of HCl into the flask • Pipette 170 µL of the Internal Standard Y from 10,000 µg/ml stock • Pipette 1.7 mL of the Internal Standard In from 10,000 µg/ml stock • Dilute to volume with Milli-Q water and mix thoroughly.

Each element is linked to an individual internal standard, refer to Table 1 for IS Assignments.

The internal standards must be within the following ranges:

Method	Control Limits	
200.7/6010B/6010C/6010D	Samples :	50%-150%
	ICSA ; ICSAB ; CCV & CCB	80%-120%

If the internal standards are out of range, the recommended action is to dilute the affected sample(s) 1:4 and reanalyze if nearby blanks indicate that the problem is matrix specific.

The iTeva software used the following calculation:

$$\text{Intensity Ratio (IR)} = \frac{\text{Intensity analyte (a)}}{\text{Intensity Internal Standard (IS)}}$$

5.2.2 Calibration Standards

Prepared with Milli-Q water that has been acidified with 1% HNO_3 and 5% HCl. The internal standards are introduced continuously to all samples (including standards and QC samples) via the peristaltic pump at an approximate 1 to 7 ratio. The calibration standards are prepared daily as follows: The Daily standard preparation will be documented on the ICAP Standard Preparation Daily Record (CHI-22-14-098).

5.2.2.1 Calibration Blank

Add ~500 mL of Milli-Q water to a 1-L Class A volumetric flask. Re-pipette 10 mL of concentrated HNO_3 and 50 mL of concentrated HCl into the flask. Dilute to volume with Milli-Q water and mix thoroughly.

5.2.2.2 Calibration Standards (Refer to Attachment 1 for element concentrations)

- The Thermo 6500 uses a blank and 5 standards for each element to calibrate the instrument. See reagent name details in Attachment 4 for reagent names in TALS.
- All calibration standards must be prepared in 1% HNO_3 and 5% HCl. To prepare the acidified water solution (S0), add 1 mL HNO_3 and 5 mL HCl per 100 mL final volume. S1 is defined as Ical Level 5, S2 is defined as Ical Level 8.

ICAP Calibration	
Standard	**Preparation**
ICAL 1 CCVL/ICVL	• Add ~500 mL of Milli-Q water to a 1000 mL Class A volumetric flask • Re-pipette 10 mL of conc. HNO_3 and 50 mL of conc. HCl into the flask. • Using Eppendorf pipettes, add 0.05 mL Bi 1000 µg/mL stock , • 1 mL TRACE MRL-CRI 1, • 1 mL TRACE MRL-CRI 2, • 0.01 mL Li 1000 µg/mL stock • Dilute to volume with Milli-Q water and mix thoroughly.
ICAL 2 CRI	• Add ~500 mL of Milli-Q water to a 1000 mL Class A volumetric flask • Re-pipette 10 mL of conc. HNO_3 and 50 mL of conc. HCl into the flask using Eppendorf pipettes, add 0.1 mL Bi 1000 µg/mL stock , • 2 mL TRACE MRL-CRI 1, • 2 mL TRACE MRL-CRI 2, • 0.02 mL Li 1000 µg/mL stock. • Dilute to volume with Milli-Q water and mix thoroughly.
ICAL 3	• 10 mL S1 + 30mL S0 (or scaled up in same proportion for larger volumes)
ICAL 4	• 20 mL S1 + 20mL S0 (or scaled up in same proportion for larger volumes)
ICAL 5 (S1)	• Add ~50 mL of Milli-Q water to a 100ml Class A volumetric flask • Re-pipette 1 mL of conc. HNO_3 and 5 mL of conc. HCl into the flask using Eppendorf pipettes, add 1.0 mL each of: ICP-MS CAL STD#1; ICP-MS CAL STD#2 • Using Eppendorf pipettes, add 0.10 mL each of: Li, Bi, Si and Ag from a 1000 µg/mL stock solution • Using an Eppendorf pipette, add 0.01 mL each of: Al and Fe from a 10000 µg/ml stock solution for Agilent 5110 only. • Dilute to volume with Milli-Q water and mix thoroughly.
ICAL 6	• 10 mL S2 + 30mL S0 (or scaled up in same proportion for larger volumes)
ICAL 7	• 20 mL S2 + 20mL S0 (or scaled up in same proportion for larger volumes)
ICAL 8 (S2)	• Add ~50 mL of Milli-Q water to a 100ml Class A volumetric flask • Re-pipette 1 mL of conc. HNO_3 and 5 mL of conc. HCl into the flask. • Using Eppendorf pipettes, add 5.0 mL of TA-CAL2 • Dilute to volume with Milli-Q water and mix thoroughly.
Ce	• To a 200 mL Class A volumetric flask filled w/ ~100 mL of Milli-Q water, add the following for each QC Solution: • 2.0 mL of concentrated HNO_3. • 10 mL of concentrated HCl. • 2.0 mL of Ce from a 1000 µg/mL stock solution. • Dilute to volume with Milli-Q water and mix thoroughly.

5.2.3 QC Solutions (Refer to Attachment 2 for element concentrations.)

Prepared with Milli-Q water that has been acidified with 1% HNO_3 and 5% HCl. All QC solutions are recorded in the TALS reagent module and are prepared as follows:

QC Solution	Preparation To a 1-L Class A volumetric flask filled w/ ~500 mL of Milli-Q water, add the following for each QC Solution:
Method Reporting Limit Check Standard (MRL)	• 10 mL of concentrated HNO_3. • 50 mL of concentrated HCl. • 1.0 mL of TA-CM-MAR19-CHI11-100 • 1.0 mL of TA-CM-MAR19-CHI12-100 • 50 uLs Bi from a 1000 µg/mL stock • 10 uLs Li from a 1000 µg/mL stock • Dilute to volume with Milli-Q water and mix thoroughly.
Initial Calibration Verification (ICV)	• 10 mL of concentrated HNO_3. • 50 mL of concentrated HCl. • 8 mL each of: CCV TA-CM-MAR19-CHI1-500 CCV TA-CM-MAR19-CHI13-500 CCV TA-CM-MAR19-CHI2-SS • 1.6 mL of 10,000 µg/mL Fe • 1.6 mL of 10,000 µg/mL Na • 1.68 mL of 10,000 µg/mL Mg • 3.6 mL of 10,000 Al • 1.84 mL of 10,000 µg/mL Ca • 3.6 mL of 10,000 µg/mL K • Dilute to volume with Milli-Q water and mix thoroughly.
Continuing Calibration Verification (CCV)	• 10 mL of concentrated HNO_3. • 50 mL of concentrated HCl. • 5 mL each of: TA-CM-MAR19-CHI-3-500 TA-CM-MAR19-CHI-4-500 TA-CM-MAR19-CHI-5 TA-CM-MAR19-CHI-6 • 4.0 mL of 1000 µg/mL Li • 0.5 mL of 1000 µg/mL Bi • 0.5 mL of 1000 µg/mL Si • 0.5 mL of 1000 µg/mL Ag • 4.5 mL of 1000 µg/mL Mn • 4.5 mL of 1000 µg/mL V • Dilute to volume with Milli-Q water and mix thoroughly.
CRI [Contract Required Detection Limit (CRDL) Standard for ICAP]	• 10 mL of concentrated HNO_3 . • 50 mL of concentrated HCl. • 2.0 mL of TA-CM-MAR19-CHI11-100 • 2.0 mL of TA-CM-MAR19-CHI12-100 • 100 uLs of 1,000 µg/mL Bi • 20 uLs of 1,000 µg/ml Li • Dilute to volume with Mill-Q water and mix thoroughly.
ICSA (Interferent Check Standard)	• 10 mL of concentrated HNO_3. • 50 mL of concentrated HCl. • 100 mL of TA-ICP-ICSA • Dilute to volume with Milli-Q water and mix thoroughly.

QC Solution	Preparation To a 1-L Class A volumetric flask filled w/ ~500 mL of Milli-Q water, add the following for each QC Solution:
ICSAB (Interferent Check Standard)	• 10 mL of concentrated HNO_3. • 50 mL of concentrated HCl. • 100 mL of TA-ICP-ICSA • 10 mL of TA-CM-MAR19-CHI10-500 • Dilute to volume with Milli-Q water and mix thoroughly.

6.0 CALIBRATION (NON-DAILY)

The following defines calibration standards/procedures that are not performed on a daily basis. Refer to Sections 7.1 & 8.0 for a listing of daily calibration standards and acceptance criteria.

6.1 Linear Range Standard (LRS)

ICAP analysis involves a Linear Dynamic Range (LDR) and a Linear Calibration Range (LCR). At Eurofins Chicago, the high standard of the LCR is set below the established upper limit of the LDR for all elements. In order to establish, verify, and document linearity at or near that upper limit, a Linear Range Study (LRS) is done every six months on each instrument. This is done by running a single standard at the upper limit of the anticipated linear range of measurement after the instrument has been calibrated in the usual daily manner. The acceptance limits for these single-element verification standards is 95-105%. During routine analysis, all results, target or non-target, that are above the LDR are flagged by the instrument software, aiding the analyst in making appropriate dilution decisions. All samples for which a target analyte or an interfering element result is found to be above the LR are diluted and re-analyzed until the concentration falls below 90% the instrument's linear range.

Note: For method 6010D, a daily linear range verification standard is run and must be within the acceptance range of 90-110%. Target and non-target interferences must be diluted below the level of the daily linear range standard. If the linear range verification standard is not run, the high standard in the calibration curve becomes the linear range.

6.2 Inter-Element Correction (IEC)

Correction factors for spectral interference will be determined at least annually for all wavelengths used for each analyte reported, any time the ICAP is adjusted in any way that may affect the IECs, or as needed based on continuing observation of Interferent Check Standard A (ICSA) and Interferent Check Standard B (ICSAB). The correction factor is calculated from the result ratios between the affected analyte and a known interferent analyzed simultaneously at an appropriately high concentration. The factor is calculated in an Excel worksheet (See attachment 5) for each instrument, documented with the instrument records, and entered into the method at the instrument PC, becoming part of the software algorithm. See Section 9.5 for additional calculation details.

For methods 200.7 and 6010D, spectral Interference Checks (SICs) for Al, Fe, Si, As, V, Co, Ti and Ca will be analyzed on a daily basis (as needed per instrument). These elements were determined to have a Ratio of Maximum Interference Concentration to RLs greater than 1 using the Eurofins Chicago ICP IEC Evaluation Spreadsheet (CA-Q-WI-092).

Correction factors for spectral interferences other than Al, Ca, Fe, and Mg are recommended and are performed as needed.

7.0 PROCEDURE

7.1 Quality Control Checks

QC Sample	Frequency[5]	Control Limit
Method Blank (MB)	1 per 20 samples	≤ Reporting Limit (LLOQ) ≤1/2 RL (LLOQ) per QAPP < MDL (Drinking water)
Lab Control Sample (LCS) [1]	1 per 20 samples	85 – 115% (200.7) 80-120% (6010B/C/D)
Matrix Spike (MS) [3,4]	1 per 10 samples (200.7) 1 per 20 samples	70 – 130% 75-125%
MS Duplicate (MSD) [3,4]	1 per 20 samples	75 – 125%; 20 RPD
Duplicates (DU) [24]	1 per 10 samples (200.7) 1 per 20 samples	20 RPD
Serial Dilution (SD) [6] (5x dilution)	1 per 10 samples (200.7) 1 per 20 samples – required if MS or MSD fails (6010D) 1 per 20 samples – required if MS or MSD fails (6010B/C)	± 10% of the original result if analyte conc. >50X MDL (200.7) ± 20% of the original result if analyte conc. >10X MDL (6010D) ± 10% of the original result if analyte conc. >10X MDL (6010B/C)
Post Digestion Spike (PDS)[7]	1 per 20 samples-recommended if SD or MS or MSD fails (200.7) 1 per 20 samples-recommended if SD or MS or MSD fails 1 per 20 samples-recommended if SD or MS or MSD fails	85-125% (200.7) 75-125% (6010B/D) 80-120% (6010C)

[1] LCS Duplicate (LCSD) is run only when required by the client or project.
[2] If ≥ 5X reporting limit, 20 RPD, if < 5X reporting limit, ± reporting limit; if < reporting limit, no control range.
[3] If sample concentration is ≤4X spike level, 70-130% for 200.7 and 75-125% for 6010B/C/D; if sample concentration is >4X spike level, no control range. If TCLP matrix spike is < 50%, Standard Addition must be performed.
[4] The sample selection for matrix QC, if not specified by the client or on the chain-of-custody, is rotated among client samples so that various matrix problems may be noted and/or addressed, pre-determined by the digestion department. Either an MS/MSD or an MS/Duplicate may be performed per batch of samples, depending on the project objectives and sample matrix.
[5] Some programs, including IDEM, require 1/10 frequency for 6010 methods.
[6] If the analyte concentration is >50X MDL, results should agree within ±10% of the original sample result.
[7] Post Digestion Spikes are required for 6010D if a high concentration sample is not available for performing the dilution test. The test only needs to be performed for the specific elements that failed the original MS limits. If the PDS is out, the sample results must be reported as estimated values. The SD and PDS are recommended, but not required per 200.7, 6010B and 6010C. Eurofins Chicago routinely runs the SD, but only runs a PDS upon client request.

7.2 Sample Preservation and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed in the method appendixes are the holding times and the references that include container and preservation requirements for compliance.

7.3 Sample Preparation

- The samples are prepared by the digestion department according to the SOP for the specific matrix type. The most commonly used digestion procedures are SW-846 Methods 3010A (waters) and 3050B (soils). Refer to UP-SP-3000 or (UP-SP-200.0) for details on sample digestion. The samples are received in the metals laboratory as 25, 50 or 100 mL final volumes.
- The turbidity is checked for all drinking water samples. If the turbidity is <1 NTU, no digestion is required.
- All samples are checked for the proper preservation at time of sample receipt. If the samples were not preserved, they are acidified and held for at least 16 hours. A sticker is affixed to the sample bottles. The pH is rechecked prior to digestion following the waiting period, and if it is greater than 2 SU, more nitric acid is added and the sample is held an additional 16 hours minimum, the pH is documented in the digestion batch in the Initial pH column of the worksheet tab.
- The pH of the drinking water sample digestates are checked prior to analysis. The documentation of this check will be recorded in the digestion batch in the sample comment field.
- The pH of the non-digested drinking water samples are checked prior to analysis. The documentation of this check will be recorded in the soluble prep batch in the sample comment field.

7.4 Calibration / Standardization

7.4.1 Instrument Set-up

Thermo ICAP 6500:
Set up the instrument with the proper operating conditions as defined in the instrument manual. The instrument must be allowed to become thermally stable (~1/2-hour) prior to calibration. A 2ppm zinc solution is aspirated to align the torch as needed. An autopeak adjust is run only if some part of the induction system is changed such as pump speed, nebulizer pressure, etc.

7.4.2 Standardization

Before any instrument is used as a measurement device, the instrument response to known reference materials must be determined. All sample measurements must be made within the linear range of the instrument. Sample analyte concentrations that are greater than 90% of the determined upper linear range (LR) must be diluted and reanalyzed.

- The Thermo 6500 uses a blank and single standard for each element to calibrate the instrument.

The calibration results are given in intensities. See the corresponding appendixes for methods for limits.

7.5 Preventive Maintenance

The required preventive maintenance is listed in the preventive maintenance logbooks which are kept at the instrument. All maintenance is recorded along with the date and the signature of the analyst performing the maintenance. Documentation of “Return to Control” must be entered into the maintenance log book. The instrument is under a full service contract with the manufacturer for all major repairs and an annual PM services. A copy of the service maintenance record must be attached to the maintenance logbook.

7.5.1 Daily Maintenance

Daily Maintenance minimally includes:

- Check / change the pump tubing for consistent sample uptake
- Check of the waste container to make sure that it doesn't overflow
- Check the tip of the torch for excessive buildup of material, clean when necessary
- Check the Nebulizer and spray chamber, clean when necessary

7.5.2 Additional Maintenance

Additional Maintenance minimally includes:

- Clean and check the water re-circulator for proper fluid level and filter cleanliness
- Vendor maintenance – attach vendor records in Maintenance Log

The instrument is under a full service contract with the manufacturer for all major repairs.

7.6 Analytical Run

After the instrument is standardized (Section 7.4.2), an analytical run is initiated. Examples of the first run of the day can found in the corresponding method appendixes:

If the CCV and CCB results are acceptable, the run may continue without re-standardization. If any of the post run QC is out-of-control, or close to being out-of-control, the instrument is re-standardized before analyzing the next digestion. Any sample with elements associated with an out-of-control CCV or CCB will be reanalyzed.

7.7 Documentation

7.7.1 Instrument Runlog

The analysis of samples and standards is documented within the instrument run log in TALs and is supported by the instrument print-out.

7.7.2 Traceability of Standards

Custom made and single element stock standard solutions which are traceable to NIST or EPA are purchased. On receipt, each standard is entered into the LIMS and is issued a unique source ID#. The manufacturer, lot #, date received, expiration date, date of verification and the initials of the recording analyst are also entered. The unique standard IDs are entered into the TALS batches along with the volumes used for spiking the various QC standards. The standard IDs appear in the TALS-generated raw data.

7.7.3 Data Review

Analytical data goes through a 200% review cycle. As results are generated, analysts review their work to ensure that the results generated meet QC requirements and relevant EPA methodologies. The analyst transfers the data into TALs in the Analyst Desktop module. Where non-compliance is observed, the analyst creates Non-Conformance Memos (NCMs) in TALs. Flags and data qualifiers can be method, project, program or QAPP specific. The analyst documents the initial review electronically within the TALs AD batch on a data review checklist (DRC) and sets the batch status in TALs to 1st level review. The second level or peer review of the data is conducted by another individual who has been trained on the review process. This secondary review is documented on the same electronic checklist, making any necessary corrections to the data or additions to the NCMs as necessary. The batch is then set to 2nd level review. The raw data is transferred into a pdf file that is attached to the AD batch in TALs. The DRC checklists are maintained as electronic files within the TALs AD batch and are retained for easy retrieval in accordance with the laboratory's record and retention policy outlined in the SOP, *UP-QA-QAM, Section 16*.

Examples of items included in the above reviews are as follows:

- QC data are outside the specified control limits for accuracy and precision
- Unusual detection limit changes are observed
- Samples having unusually high results
- Samples exceeding a known regulatory limit
- Raw data indicating some type of contamination or poor technique
- Inconsistent peak integration (if applicable)
- Transcription errors
- Results outside of calibration range

8.0 QUALITY CONTROL

8.1 QC Summary

NOTE: The following laboratory acceptance criteria are set as default control limits. Statistical limits are generated on an annual basis from cumulative LCS data and can be implemented when specified by the client, contract, or QAP.

8.1.1 Method Blank (MB)

At least one MB will be included in each laboratory lot of 20 or fewer samples. This QC sample will be in an aqueous media. An MB is analyzed to determine if contaminants are being introduced into the sample during the sample preparation procedures.

8.1.2 Laboratory Control Sample (LCS)

At least one LCS will be included in each laboratory lot of 20 or fewer samples. This QC sample will be in an aqueous media. LCSs are analyzed to determine the accuracy of the digestion process. Accuracy will be measured by the percent recovery (%R) of the LCS. If the results are outside these control limits, all samples in the preparation set must be re-digested and reanalyzed. See Attachment 4 for element concentrations.

8.1.3 Matrix Spike (MS) / Matrix Spike Duplicate (MSD) / Matrix Duplicate (DU)

Method	Frequency	Recovery Range	RPD
200.7	10% (1 in 10 samples)	70-130	20
6010B/C/D	5% (1 in 20 samples)	75-125	20

TCLP - If the MS recovery is <50% and the concentration does not exceed the regulatory limit or the sample concentration is within 20% of the regulation level, the Method of Standard Addition (MSA) is required. Three aliquots of the sample are spiked at 50%, 100% and 150% of the sample concentration or, if the sample concentration is < RL, the MSA is at 50%, 100% and 150% of the MS level. The data is subjected to linear regression whereas the concentration of the unknown is the x-intercept and the correlation coefficient value must be ≥ 0.995.

8.1.4 Internal Standard Controls

The internal standard intensity counts for the calibration blank are recorded in the ICP runlog. Control limits based on 3 Standard Deviations of the mean are established on a monthly basis. If an out-of-control situation occurs, attempts will be made to explain and correct the problem. If the instrument operating conditions are changed or components replaced that require optimization, new control limits will be established.

8.1.5 Serial Dilution

Method	Frequency	>MDL/RL	Agree range
6010B/C	5% (1 in 20 samples)	>10 time MDL	±10%
6010D	5% (1 in 20 samples)	>25 time LLOQ (RL)	±20%

8.1.6 Post Digestion Spikes

A Post Digestion Spike may be analyzed to compensate for the matrix effect. Post Digestion Spikes are analyzed on a project, program or client request basis.

Method	Recovery
6010B/D	75-125%
6010C	80-120%

8.2 Corrective Actions

When an out-of-control situation occurs, the analysts must use his/her best analytical judgment and available resources to determine the corrective action to be taken. The out-of-control situation may be caused by more than one variable. The analyst should seek the assistance of his/her supervisor, section manager, QA personnel, or other experienced staff if he/she is uncertain of the cause of the out-of-control situation. The analysis must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out-of-control situation should be reanalyzed. Out-of-control data must never be released without approval of the supervisor, section manager, project manager, QA personnel or the laboratory manager.

The following steps must be taken when an out-of-control situation occurs:

- demonstrate that all the problems creating the out-of-control situation were addressed;
- document the problem and the action which was taken to correct the problem on a Non-Conformance Memo (NCM);
- document on the NCM that an in-control situation has been achieved; and

- receive approval of the supervisor, section manager, project manager, QA personnel, or the laboratory manager prior to the release of any analytical data associated with the problem.

QC Indicator	Suggested Corrective Actions
Calibration Curve	• reanalyze the standard curve; • prepare new stock and/or working standards; • check reagents/solutions and prepare fresh if necessary.
ICV/ICVL[3]	• repeat the ICV to verify proper preparation; • prepare a new ICV from original stock; • recalibrate with a new standard curve; • prepare a new stock and/or working standards; • check the reagents/solutions and prepare fresh if necessary. • any exceedance of the ICVL method limits of 70-130% recovery requires and NCM and approval of the project manager prior to acceptance and the reporting of the data to the client. The 60-140% alternate limit will be used only if approval from the project manger is obtained otherwise re-analysis of the samples associated with a failed ICVL is mandatory.
ICB	• prepare new ICB to verify proper preparation; • verify that the instrument base-line is stable and perform necessary maintenance, cleaning, etc.., to achieve stability; • determine the source of contamination by the process of elimination, carryover from a previous analysis or reagent contamination and correct the problem; • check reagents/solutions and prepare fresh if necessary; • correct for any contamination and reanalyze ICB and any associated samples.
ICSA / ICSAB[1]	• reanalyze to verify; • verify that the instrument is stable and perform any additional maintenance or warm-up as necessary; • check reagents and prepare fresh if necessary; • update inter-element correction factors, if needed.
LCS	<u>If LCS is low:</u> • reanalyze to verify that it is out-of-control; • determine the source of error within the preparation procedure, repeat the sample set, write a NCM. <u>If the LCS is high:</u> • reanalyze to verify that it is out-of-control; • determine the source of error within the preparation procedure, repeat the sample set; • determine if the high result is due to contamination; • check for contamination of reagents, LCS stock solution, or preparation area; • correct for contamination, reanalyze.
MB	• reanalyze to verify that it is beyond the reporting limit; • determine the source of contamination; • determine if the high result is due to contamination; • check for contamination of reagents or preparation area; • correct for contamination, reanalyze set; • in the extreme case where all samples in the set are at least 10X >MB, reanalysis will not be required. However, a NCM will be written and approved by the supervisor or department manager.
DU or MS/MSD	• an NCM must be written describing the out-of-control situation. The supervisor or section manager will review the NCM and decide if re-digestion is necessary; • a post matrix spike will be performed for all out-of-control MSs.

QC Indicator	Suggested Corrective Actions
Serial Dilution (SD)[2]	• prepare a new serial dilution to verify proper preparation; • an NCM will be written and approved by the supervisor or section manager.
Post Digestion Spike (PDS)[5]	• Flag and report data as estimated values
CCV/CCVL[4]	• repeat the CCV to verify proper preparation; • prepare a new CCV from the original stock; • check for instrument base-line drift or a change in one or more of the reagents; • check the reagents/solutions and prepare fresh if necessary; • recalibrate with a new standard curve and repeat all samples since the previous in control CCV; • never dispose of any samples until you are sure that all QC are within the control limits. • any exceedance of the CCVL method limits of 70-130% recovery requires and NCM and approval of the project manager prior to acceptance and the reporting of the data to the client. The 60-140% alternate limit will be used only if approval from the project manger is obtained otherwise re-analysis of the samples associated with a failed CCVL is mandatory.
CCB	• prepare a new CCB to verify proper preparation; • verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc.., to achieve stability; • determine the source of contamination by the process of elimination, carryover from a previous analysis or reagent contamination and correct the problem; • check reagents/solutions and prepare fresh if necessary; • correct for any contamination and reanalyze the CCB and any associated samples; • never dispose of any samples until you are sure that all QC, especially the CCB are within the control limits.
Linear Range Check[5]	• Target and non-target interferences must be diluted below the level of the daily linear range standard. If the linear range verification standard is not run, the high standard in the calibration curve becomes the linear range.
Additional CAs	• If any of the ICV, ICB, CCV or CCB results are out-of-control for any element, the instrument is restandardized and the samples associated with the out-of-control elements are reanalyzed. • If the MB or LCS is out-of-control for any element, the samples are redigested. An exception is if the sample concentrations are ≥10X the MB contamination or < reporting limit, the results are reported as is. • If any of the MDs or MSs are out-of-control, the client is notified of the poor results via a case narrative that is sent with the data report.
Pre-formatted NCMs are available for multiple likely data quality occurrences. NCMs are completed by the analyst performing the analysis/initial review. The NCM is then reviewed the supervisor, department manager, and/or project manager.	

[1]-for method 200.7
[2]-for method 6010B
[3]-ICVL is for 6010C and 6010D only
[4]-CCVL is for 6010C only
[5]-for method 6010D only

9.0 CALCULATIONS

The sample results are stored in a data file on the desktop computer. The data are copied directly to the analyst desktop module (ADII) in TALS. Direct transfer of the data file eliminates transcription errors since the data is not entered by hand.

The QC calculations and all corrections for weight, volume, dilution factor, and moisture are performed by TALS in ADII. The data for each individual job in each batch are evaluated automatically according to limits set up in TALS by the project managers and the QAM. Project or job-specific flags and qualifiers are applied automatically, but must be reviewed.

9.1 Accuracy

9.1.1 ICV, CCV, or LCS % Recovery

$$\frac{\text{observed concentration}}{\text{actual concentration}} \times 100$$

9.1.2 MS % Recovery

$$\frac{(\text{spiked sample}) - (\text{unspiked sample})}{\text{spike concentration}} \times 100$$

9.2 Precision

9.2.1 DU Relative Percent Difference (RPD)

$$\frac{|\text{orig.sample value} - \text{dup sample value}|}{\left[\frac{\text{orig.sample value} + \text{dup.sample value}}{2}\right]} \times 100$$

9.3 Concentration

$$\frac{\text{mg}}{\text{kg}} \text{ or } \text{L} = \frac{\text{C} \times \text{V} \times \text{D}}{\text{W}}$$

Where:
C = sample concentration in extract (ppm)
V = Volume of extract (mL)
D = Dilution Factor
W = Weight/Volume of sample aliquot extracted (grams or mL)

NOTE: All dry weight corrections are made in the LIMs analytical batch at the time the result is calculated.

9.4 Calculations for SiO2 and Hardness

Calculation of SiO2

(Si) Silicon Raw (mg/L) × 2.1392 × PF
PF=Prep Factor

Calculation of Magnesium Hardness

(Mg) Magnesium Raw (mg/L) × 4.118 × PF

Calculation of Calcium Hardness

(Ca) Calcium Raw (mg/L) × 2.497 × PF

Calculation of Total Hardness

((Calcium Raw (mg/L) × 2.497) + (Magnesium Raw (mg/L) × 4.118)) × PF
Final units appropriate to reporting requirements.

Note: All the raw data associated with the calculation of the Total Hardness results resides within the ICP analytical batch where the Ca and Mg results are analyzed for each sample. All QC associated with the Ca and Mg are calculated, evaluated and must meet acceptance criteria before the Total Hardness results can be calculated and reported. The Total Hardness method in TALs is a calculation method only that imports the Ca and Mg final results obtained from the 200.7 or 6010D analytical batch and performs the calculation.

9.5 Calculation of Inter-element Correction Factors

Spike a blank with the known interfering element at an appropriate concentration, typically at the upper level of the linear range. Divide the observed result of the affected element by the observed result of the interfering element. Since the IEC study was done with the previous IEC factor applied, add (or subtract if negative) this result to the current correction factor value in the instrument software. The result is the new IEC for the affected element, equal to the adjustment made on 1 ppm of the affected element.

9.5.1 Spectral Interference Check (SIC) Evaluation

Ratio of Maximum Interference Concentration to RLs

$$\left[\frac{\text{Apparent analyte}}{\text{RL}}\right] \text{at maxium interferent concentration} = \left(k \times \frac{\text{LR}}{\text{RL}}\right)$$

k = k-Value for Interferent
LR = Linear Range of Interferent
RL = Reporting Limit of Affected Analyte

10.0 POLLUTION CONTROL

It is Eurofins Chicago's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

10.1 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to UP-WM-001.

The following waste streams are produced when this method is carried out.

- Waste from this procedure will enter the “Corrosive Wastewater” wastestream.

11.0 METHOD PERFORMANCE CRITERIA

Refer to sections 1, 6, 7 and 8.

12.0 REFERENCES

Refer to Section 1.0.

13.0 ATTACHMENTS

Table 1. Element - Reporting Limits and IS Assignments

Attachment 1. Standard Stock Solutions (S1A, S1B, S1, S2A, S2B, S2)
Attachment 2. Stock QC Solutions (ICV/CCV, CRI, ICSA/ICSAB)
Attachment 3. Laboratory Control Standard (LCS) / Matrix Spike (MS/MSD) Concentrations

Appendix 1. Method 200.7
Appendix 2. Method 6010B
Appendix 3. Method 6010C
Appendix 4. Method 6010D

14.0 REVISION HISTORY

- Revision 00 updated on 08/01/23
- Combined SOPs UP-ME-200.7, UP-ME-6010B, UP-ME-6010C, and UP-ME-6010D

Table 1.

Element - Reporting Limits and IS Assignments

Element	ICAP 6500 Wavelength (nm)	ICAP 6500 Internal Standard	Reporting Limit (RL)[1] (µg/L)	Default (200.7) RL [2] (µg/L)	Reporting Limit (Soils) (mg/kg)
Al	308.2	Y 371.0	200	100	20.0
Sb	206.8	Y 224.3	20	10	2.0
As	189.0	Y 224.3	10	5	1.0
Ba	455.4	Y 371.0	10	5	1.0
Be	234.8	Y 371.0	4	2	0.40
Bi	223.0	In 230.6	50	25	2.0
B	208.9	Y 224.3	50	25	5.0
Ca	317.9	Y 371.0	200	100	20.0
Cd	228.8	Y 224.3	2	1	0.20
Cr	267.7	Y 360.0	10	5	1.0
Co	228.6	In 230.6	5	2.5	0.50
Cu	324.7	Y 360.0	10	5	1.0
Fe	271.4	Y 371.0	200	100	20.0
Pb	220.3	In 230.6	5	2.5	0.5
Mg	279.0	Y 371.0	100	50	1.0
Mn	257.6	Y 371.0	10	5	10.0
Mo	202.0	Y 224.3	10	5	1.0
Ni	231.6	In 230.6	10	5	1.0
K	766.4	Y 371.0	500	250	1.0
Li	670.7	Y 371.0	10	5	50.0
Se	196.0	Y 224.3	10	5	1.0
Si	212.4	Y 224.3	200	100	20.0
Ag	328.0	Y 360.0	5	2.5	0.50
Na	589.5	Y 371.0	1,000	500	100
Sr	421.5	Y 360.0	5	2.5	0.50
Tl	190.8	In 230.6	10	5	1.0
Sn	189.9	In 230.6	40	20	4.0
Ti	334.9	Y 360.0	5	2.5	0.50
V	292.4	Y 360.0	5	2.5	0.50
Zn	206.2	In 230.6	20	10	2.0
Y [3]	224.3/360.0/371.0		N/A	N/A	N/A
In[3]	230.6		N/A	N/A	N/A

[1] These are routine ICAP reporting limits (RL). Lower RLs may be available to use per client request. Sample RLs will vary depending on sample volume, dilution factors, and changes in MDLs. Contact the laboratory for the most current RLs based on annual MDL determinations.
[2] 'Default' 200.7 RLs are ½ the listed values due to the concentration of the sample at the digestion step.
[3] Y and In on the ICAP 6500, are used as internal standards and are introduced continuously to all samples (including standards and QC samples) via the peristaltic pump at an approximate 1 to 7 ratio.

Attachment 1

Calibration Stock Standard Solutions

Vendor	Stock Name	Element	Conc. (mg/L)	S1 mg/L	S2 mg/L
CPI International	TA-CM-MAR19-CHI4-500	Sb	100	1	
		Mo	100	1	
		Sn	100	1	
		Ti	100	1	
CPI International	TA-CM-MAR19-CHI3-500	As	100	1	
		Ba	100	1	
		Be	100	1	
		B-	100	1	
		Cd	100	1	
		Co	100	1	
		Cr	100	1	
		Cu	100	1	
		Mn	100	1	
		Ni	100	1	
		Pb	100	1	
		Se	100	1	
		Sr	100	1	
		Tl	100	1	
		V-	100	1	
		Zn	100	1	
CPI International	4400-1000061 TA-1000504F TA-1000511	Bi	1000	1	
		Si	1000	1	
		Ag	1000	1	
CPI International	TA-CM-MAR19-CHI5	Al	10,000	25	100
		K	10,000	25	100
CPI International	TA-CM-MAR19-CHI6	Ca	5,000	25	100
		Fe	5,000	25	100
		Mg	5,000	25	100
		Na	5,000	25	100
CPI International	TA-1000291	Li	1000	1	

Note: Vendors and stock names may vary.

Attachment 2.

Example of Stock QC Solutions

Vendor	Stock Name	Element	Conc. (mg/L)	ICV (mg/L)	CCV (mg/L)
CPI International	TA-CM-MAR19-CHI1-500	As	50	0.4	0.5
		B	50	0.4	0.5
		Ba	50	0.4	0.5
		Be	50	0.4	0.5
		Bi	50	0.4	0.5
		Cd	50	0.4	0.5
		Co	50	0.4	0.5
		Cr	50	0.4	0.5
		Cu	50	0.4	0.5
		Ni	50	0.4	0.5
		Pb	50	0.4	0.5
		Se	50	0.4	0.5
		Fe	500	20	25
		Mn	500	4	5
		V	500	4	5
		Tl	50	0.4	0.5
		Zn	50	0.4	0.5
		Sr	50	0.4	0.5
CPI International	TA-CM-MAR19-CHI13-500	Ca	200	20	25
		Na	500	20	25
		Al	500	40	50
		Mg	400	20	25
		K	500	40	50
		Li	400	3	4
CPI International	TA-CM-MAR19-CHI12-SS	Ag	50	0.4	0.5
		Sb	50	0.4	0.5
		Mo	50	0.4	0.5
		Si	50	0.4	0.5
		Sn	50	0.4	0.5
		Ti	50	0.4	0.5
CPI International	Single Elements * spiked on top of custom mixes.	Al	10,000	40	50
		Ca	10,000	20	25
		Fe	10,000	20	25
		Na	10,000	20	25
		K	10,000	40	50
		Mg	10,000	20	25

Note: Vendors and stock names may vary.

Attachment 2.
(continued)
Example of Stock QC Solutions

Vendor	Stock Name	Element	Conc. (mg/L)	ICVL Conc. (mg/L)	CRI Conc. (mg/L)
CPI	TA-CM-MAR19-CHI11-100	Al	200	0.200	0.400
International	TA-CM-MAR19-CHI12-100	Sb	20	0.020	0.040
	TA-CM-MAR19-CHI11-100	As	10	0.010	0.020
	TA-CM-MAR19-CHI11-100	Ba	10	0.010	0.020
	TA-CM-MAR19-CHI11-100	Be	4	0.0040	0.008
	Bi Stock	Bi	1,000	0.020	0.040
	TA-CM-MAR19-CHI11-100	B	50	0.050	0.100
	TA-CM-MAR19-CHI11-100	Cd	2	0.0020	0.0040
	TA-CM-MAR19-CHI11-100	Ca	200	0.200	0.400
	TA-CM-MAR19-CHI11-100	Cr	10	0.010	0.020
	TA-CM-MAR19-CHI11-100	Co	5	0.0050	0.010
	TA-CM-MAR19-CHI11-100	Cu	10	0.010	0.020
	TA-CM-MAR19-CHI11-100	Fe	200	0.20	0.40
	TA-CM-MAR19-CHI11-100	Pb	5	0.0050	0.010
	TA-CM-MAR19-CHI11-100	Mg	100	0.10	0.20
	TA-CM-MAR19-CHI11-100	Mn	10	0.010	0.020
	TA-CM-MAR19-CHI12-100	Mo	10	0.010	0.020
	TA-CM-MAR19-CHI11-100	Ni	10	0.010	0.020
	TA-CM-MAR19-CHI11-100	K	500	0.500	1.00
	TA-CM-MAR19-CHI11-100	Se	10	0.010	0.020
	TA-CM-MAR19-CHI12-100	Si	200	0.20	0.40
	TA-CM-MAR19-CHI11-100	Ag	5	0.0050	0.010
	TA-CM-MAR19-CHI11-100	Na	1000	1.00	2.00
	TA-CM-MAR19-CHI11-100	Sr	5	0.0050	0.010
	TA-CM-MAR19-CHI11-100	Tl	10	0.010	0.020
	TA-CM-MAR19-CHI12-100	Sn	40	0.040	0.080
	TA-CM-MAR19-CHI12-100	Ti	5	0.0050	0.010
	TA-CM-MAR19-CHI11-100	V	5	0.0050	0.010
	TA-CM-MAR19-CHI11-100	Zn	20	0.020	0.040

Attachment 2.
(continued)
Example of Stock QC Solutions

Vendor	Stock Name	Element	Conc. (mg/L)	ICSA Conc. (mg/L)
CPI International	TA-ICP-ICSA	Al	5,000	500
		Ca	5,000	500
		Mg	5,000	500
		Fe	2,000	200
				ICSAB Conc. (mg/L)
CPI International	TA-ICP-ICSA	Al	5,000	500
		Ca	5,000	500
		Mg	5,000	500
		Fe	2,000	200
CPI International	TA-CM-MAR19-CHI10-500	Cd	100	1
		Ni	100	1
		Zn	100	1
		Sb	60	0.6
		Ba	50	0.5
		Be	50	0.5
		Co	50	0.5
		Cr	50	0.5
		Cu	50	0.5
		Mn	50	0.5
		V	50	0.5
		Ag	20	0.2
		As, Tl	10	0.1
		Pb, Se	5	0.05
CPI International	SIC Spectral Interferent Solutions (Individual)	Al	600	
		Fe	500	
		Si	100	
		As	1.0	
		V	7.0	
		Ca	600	
		Ti	3.0	
		Co	3.0	
		Cu	20.0	
		Mo	2.0	
		Sn	10.0	

NOTE: Vendors, stock names and purchased concentrations may vary.

Attachment 2.
(continued)
Stock QC Solutions

Vendor	Stock Name	Element	Conc. (mg/L)	Daily Linear Range Std mg/L
CPI	Aluminum	Al	*See ICSA*	600 (ICSA)
International	Antimony	Sb	1,000	20
	Arsenic	As	1,000	1.0
	Barium	Ba	1,000	7.5
	Beryllium	Be	1,000	10
	Bismuth[1]	Bi	1,000	5
	Boron	B	1,000	50
	Cadmium	Cd	1,000	10
	Calcium	Ca	*See ICSA*	600 (ICSA)
	Chromium	Cr	1,000	2.0
	Cobalt	Co	1,000	2.0
	Copper	Cu	1,000	2.0
	Iron	Fe	*See ICSA*	500 (ICSA)
	Lead	Pb	1,000	100
	Lithium[2]	Li	100	10
	Magnesium	Mg	*See ICSA*	600 (ICSA)
	Manganese	Mn	1,000	20
	Molybdenum	Mo	1,000	1.0
	Nickel	Ni	1,000	20
	Potassium	K	*See S2/10,000*	100 (S2) / 750
	Selenium	Se	1,000	20
	Silicon	Si	1,000	100
	Silver	Ag	*See S1*	1.0 (S1) / 1.0
	Sodium	Na	*See S2*/10,000	50 (S2) / 750
	Strontium	Sr	*See S1*	1 (S1) / 2.0
	Thallium	Tl	1,000	10
	Tin	Sn	1,000	10
	Titanium	Ti	1,000	2.0
	Vanadium	V	1,000	2.5
	Zinc	Zn	1,000	20

Attachment 3.

Known Digested QC Values (mg/L)

Element	LCS/Matrix Spike
Al	2
Sb	0.5
As	0.1
Ba	2
Be	0.05
Bi	0.5
B	1
Cd	0.05
Ca	10
Cr	0.2
Co	0.5
Cu	0.25
Fe	1
Pb	0.1
Li	0.5
Mg	10
Mn	0.5
Mo	1
Ni	0.5
K	10
Se	0.1
Si	5
Ag	0.05
Na	10
Sr	1
Tl	0.1
Sn	1
Ti	1
V	0.5
Zn	0.5

Default Control Limits

Method	Type	Recovery
200.7	LCS	85-115%
	Matrix Spike	70-130%
6010B/C/D	LCS	80-120%
	Matrix Spike	75-125%
	TCLP Spike	>50%

Appendix 1: 200.7

Standardization:

Standard	Frequency	Control Limit
Calibration Curve	Initially	Corr. Coeff. ≥ 0.995
High Standards (S1, S2)	After the Calibration Curve	± 5% of the Known Conc.
Initial Cal. Verif. (ICV)	After the Calibration Curve	± 5% of the Known Conc. < 3% RSD
Initial. Cal. Blank (ICB)	After the ICV	≤ Reporting Limit; (≤ ½ RL per QAPP)
MRL	After the ICB; Prior to sample analysis	None Required
CRI	Daily, once per run	None Required
ICSA / ICSAB	Daily, once per run	± 20% of the Known Conc. or < RL for non-spiked elements
Cont. Cal. Verif. (CCV)	Every 10 reading; End of each run	± 10% of the Known Conc.
Cont. Cal. Blank (CCB)	Every 10 readings; End of each run	≤ Reporting Limit; (≤ ½ RL per QAPP)

After the instrument is standardized (Section 7.4.2, after 5 point calibration), an analytical run is initiated. The first run of the day would proceed as follows:

- ICV Initial Calibration Verification
- ICB Initial Calibration Blank
- ICVL Low-level ICV
- ICSA Interferent Check Standard A
- ICSAB Interferent Check Standard B
- CCV Continuing Calibration Verification
- CCB Continuing Calibration Blank
- MRL(1) Check Standard at the standard reporting limit (per QAPP)
- LRC Linear Range Check Standard (per Project\QAPP requirement)
- MB (2) Method Blank
- LCS (3) Laboratory Control Sample
- Sample 1 (4)
- Sample 1 (5) Serial Dilution (5X Dilution)
- Sample 1 (6) Matrix Duplicate
- Sample 1 (7) Matrix Spike
- Sample 2 (8)
- . (9)
- . (10)
- CCV Continuing Calibration Verification
- CCB Continuing Calibration Blank
- SIC Checks Al, Fe, Si, As, V, Co, Ti and Ca (as needed per instrument) at the end of the run, unless needed for IEC calculation.

Appendix 2: 6010B

Standardization:

Standard	Frequency	Control Limit
Calibration Curve	Initially	Corr. Coeff. ≥ 0.995
High Standards (S1, S2)	After the Calibration Curve	± 5% of the Known Conc.
Initial Cal. Verif. (ICV)	After the Calibration Curve	± 10% of the Known Conc. <5% RSD
Initial. Cal. Blank (ICB)	After the ICV	≤Reporting Limit ≤1/2 RL per QAPP
CRI	Daily	None Required
MRL	Daily in DoD batches	80-120%
ICSA / ICSAB	Daily	*± 20% of the Known Conc. or absolute value <RL for all non-spiked elements. <1/2 RL per QAPP
Cont. Cal. Verif. (CCV)	Every 10 reading; End of each run	± 10% of the Known Conc.
Cont. Cal. Blank (CCB)	Every 10 readings; End of each run	≤Reporting Limit ≤ ½ RL per QAPP

* Note: Samples with extremely high “A” concentrations and low “B” concentrations may warrant further evaluation.

After the instrument is standardized (Section 7.4.2, after 5 point calibration), an analytical run is initiated. The first run of the day would proceed as follows:

- ICV Initial Calibration Verification
- ICB Initial Calibration Blank
- CRI Spiked Blank Sample
- ICSA Interferent Check Standard A
- ICSAB Interferent Check Standard B
- CCV Continuing Calibration Verification
- CCB Continuing Calibration Blank
- MRL Spiked Blank Sample (DoD)
- MB (1) Method Blank
- LCS (2) Laboratory Control Sample
- Sample (3)
- Sample (4) Serial Dilution (SD)
- Sample (5) Matrix Duplicate (DU)
- Sample (6) Matrix Spike (MS)
- Sample (7) Matrix Spike Duplicate (MSD)
- Sample (8)
- Sample (9)
- Sample (10)
- CCV Continuing Calibration Verification
- CCB Continuing Calibration Blank

Appendix 3: 6010C

Standardization:

Standard	Frequency	Control Limit
Calibration Curve	Initially	Corr. Coeff. ≥ 0.998
High Standards (S1, S2)	After the Calibration Curve	± 5% of the Known Conc.
Initial Cal. Verif. (ICV)	After the Calibration Curve – mid-range	± 10% of the Known Conc. <5% RSD
Low-level ICV (ICVL)	After mid-range ICV - RL level	± 30% of Known Conc.
Initial. Cal. Blank (ICB)	After the ICV	≤ Reporting Limit ≤ ½ RL per QAPP
ICSA / ICSAB	Daily	*± 20% of the Known Conc. or absolute value <RL for all non-spiked elements. < ½ RL per QAPP
Cont. Cal. Verif. (CCV)	Every 10 reading; End of each run – mid-range	± 10% of the Known Conc.
Low-level CCV (CCVL)	After mid-range CCV – at RL	± 30% of Known Conc.
Cont. Cal. Blank (CCB)	Every 10 readings; End of each run	≤ Reporting Limit ≤1/2 RL per QAPP

* Note: Samples with extremely high "A" concentrations and low "B" concentrations may warrant further evaluation.
The Low-level ICV and Low-level CCV are only required at the beginning and the end of a run, but may be run with every CCV since reported data must be successfully bracketed. Any exceedance of the ICVL / CCVL method limits of 70-130% recovery requires and NCM and approval of the project manager prior to acceptance and the reporting of the data to the client. The 60-140% alternate limit will be used only if approval from the project manager is obtained otherwise re-analysis of the samples associated with a failed ICVL/CCVL is mandatory.

After the instrument is standardized (Section 7.4.2, after 5 point calibration), an analytical run is initiated. The first run of the day would proceed as follows:

- ICV Initial Calibration Verification
- ICB Initial Calibration Blank
- ICVL Low-level ICV
- ICSA Interferent Check Standard A
- ICSAB Interferent Check Standard B
- CCV Continuing Calibration Verification
- CCB Continuing Calibration Blank
- MB (1) Method Blank
- LCS (2) Laboratory Control Sample
- Sample (3)
- Sample (4) Serial Dilution (SD)
- Sample (5) Matrix Duplicate (DU)
- Sample (6) Matrix Spike (MS)
- Sample (7) Matrix Spike Duplicate (MSD)
- Sample (8)
- Sample (9)
- Sample (10)
- CCV Continuing Calibration Verification
- CCB Continuing Calibration Blank
- CCVL Low-level CCV

Appendix 4: 6010D

Standardization:

Standard	Frequency	Control Limit
Calibration Curve	Initially	Corr. Coeff. (r) ≥ 0.995
High Standards (S1, S2)	After the Calibration Curve	± 5% of the Known Conc.
Initial Cal. Verif. (ICV)	After the Calibration Curve – mid-range	± 10% of the Known Conc. <5% RSD
Low-level ICV (ICVL)	After mid-range ICV - RL level	± 20% of Known Conc.
Initial. Cal. Blank (ICB)	After the ICV	≤ ½ Reporting Limit (LLOQ)
ICSA	Daily immediately after calibration	± 20% of the Known Conc. or the absolute value < 2x RL (LLOQ) for all non-spiked elements. < ½ RL per QAPP
Cont. Cal. Verif. (CCV)	Every 10 reading; End of each run – mid-range	± 10% of the Known Conc.
Cont. Cal. Blank (CCB)	Every 10 readings; End of each run	≤ Reporting Limit (LLOQ) ≤1/2 RL (LLOQ) per QAPP
Linear Range Verification Standard	Daily[1]	± 10% of the Known Conc

[1]Target and non-target interferences must be diluted below the level of the daily linear range standard. If the linear range verification standard is not run, the high standard in the calibration curve becomes the linear range.

After the instrument is standardized (Section 7.4.2, after 5 point calibration), an analytical run is initiated. The first run of the day would proceed as follows:

- ICV — Initial Calibration Verification
- ICB — Initial Calibration Blank
- ICVL — Low-level ICV
- ICSA — Interferent Check Standard A
- CCV — Continuing Calibration Verification
- CCB — Continuing Calibration Blank
- MRL(1) — Check Standard at the standard reporting limit (per QAPP)
- LRC — Linear Range Check Standard
- MB (2) — Method Blank
- LCS (3) — Laboratory Control Sample
- Sample (4)
- Sample (5) — Serial Dilution (SD)
- Sample (6) — Matrix Duplicate (DU)
- Sample (7) — Matrix Spike (MS)
- Sample (8) — Matrix Spike Duplicate (MSD)
- Sample (9)
- Sample (10)
- CCV — Continuing Calibration Verification
- CCB — Continuing Calibration Blank
- SIC Checks — Al, Fe, Si, As, V, Co, Ti and Ca (as needed per instrument) at the end of the run, unless needed for IEC calculation.

TITLE: Metals Analysis Inductively Coupled Argon Plasma / Mass Spectrometry by EPA 200.8 rev5.4, 6020, 6020A, or 6020B

Approvals (Signature/Date):

Debbie Johnson 5/10/24
Debbie Johnson Date
Supervisor, Metals Department

Chris Hoham 5/10/24
Chris Hoham Date
Env. Health & Safety Coor.

Nicole Berg 5/10/24
Nicole Berg Date
Quality Assurance Manager

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1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) outlines the guidelines for determining metal concentrations by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). This SOP was written using EPA Method 200.8 Version 5.4, EPA methods 6020A and 6020B as a reference. The hardness calculations found in Section 9.4 are from Standard Methods, 18th, 20th, and 23rd Editions, method 2340 B.

Clients may request slight modifications to this SOP for non-drinking water samples. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check, PT/QC sample) verified prior to implementation. Any modifications are written into a Quality Assurance Plan (QAP) and authorized via laboratory signature approval. Modifications may be subsequently addressed in the report case narrative. **Note: There are no method modifications allowed for Drinking Water samples without prior written approval from US EPA.**

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants" with additional details are provided in the Eurofins Corporate SOP, *NDSC-QA-SOP42091, Detection Limits,* and the Eurofins Chicago SOP, *UP-QA-017, Method Detection Limit Studies.* MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; the MDL study will be performed and verified on an annual basis, verifying the Lower Limit of Quantitation (LLOQ) for the method.

1.1.2 Demonstration of Capability

Before the laboratory may institute a new method and begin reporting results, the laboratory shall confirm that it can properly operate the method. A demonstration of capability is performed whenever there is a change in instrument type, method or personnel. An Initial Demonstration of Capability (IDOC) must be thoroughly documented and approved by the Department Manager/Supervisor and QA Manager prior to independently analyzing client samples. All associated documentation must be retained in the QA Department and in the Analyst Training files. For additional details on the demonstration of capability procedures followed, refer to the laboratory SOP, *UP-QA-QAM, Quality Assurance Manual, Sections 19.4.2 and 19.4.3.*

1.1.3 Instrument Detection Limits

Instrument Detection Limits (IDLs) are performed on an annual basis for each element and for each instrument. The IDLs can be estimated as the mean of the blank results plus three times the standard deviation of 10 replicate analyses of the reagent blank solution. These limits are used to gauge both instrument sensitivity and instrument performance. Note: IDLs are also required after major maintenance such as changing the detector on the instrument.

1.1.4 Reporting Limits (LLOQ)

Reporting Limits (LLOQ) are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. The laboratory maintains reporting limits that are higher than the MDL.

Wherever possible, reporting is limited to values ~3-5x the respective MDL to ensure confidence in the value reported. Client specific requests for reporting to the MDL are special circumstances not to be confused with the previous statement. Refer to Table 1 for element isotopes and routine reporting limits, uncorrected for dilution factors, sample weight/volume variances, or moisture content.

1.1.5 Definitions

Refer to Section 3.0 of the Laboratory's Quality Assurance Manual (UP-QA-QAM).

2.0 INTERFERENCES

Physical and Chemical Interferences are the main interferences that are commonly present on the ICP-MS.

2.1 Physical Interferences

Physical interferences are usually associated with sample uptake and nebulization processes. These interferences can usually be eliminated by using a peristaltic pump which assures a constant sample uptake rate. The use of internal standard can be used to correct for physical interferences. If a sample is extremely viscous or contains a very high dissolved solids concentration, a dilution of the sample may be required to assure a constant and smooth nebulization rate. The recommended dilution is a fivefold dilution (1:4).

Memory interferences, or carry-over, are caused by large sample concentrations. These samples can cause deposits on the sample and skimmer cones, spray chamber and nebulizer. The rinse time must be long enough to eliminate this.

2.2 Chemical Interferences

Chemical interferences are highly dependent on the sample matrix type and the element. These interferences include ionization effects and molecular compound formation.

2.2.1 Isobaric elemental interferences

These interferences are caused by isotopes of the different elements forming ions with the same atomic mass which cannot be resolved by the mass spectrometer. Elemental Correction Factors are used to correct these interferences. Standard correction factors are available from a database supplied by the manufacturer of the instrument, however they may be manually changed by the analyst based on local conditions. If a change is made, it must be reviewed by another analyst and documented in the maintenance log. If a significant interference problem occurs in a sample, the sample may need to be reanalyzed using a different isotope.

2.2.2 Isobaric Molecular and Doubly–charged interferences

Most of these interferences have been identified and are interferences consisting of more than one atom or charge. These include polyatomic ions and doubly charged ions. The polyatomic ions include the Oxides, Argides and Hydrides. An argide example is 75ArCl on the 75As mass signal. Oxide interference can be minimized from tuning the instrument. Positioning of the torch and nebulizer gas flow will have the greatest effect. Argide interference can be reduced by using Collision Cell Technology (CCT). Collision Cell Technology is accomplished by adding an auxillary gas into the lens chamber. A Hydrogen/Helium gas mixture is used on Thermo ICPMS. Helium is used on the Agilent ICPMS. This gas mixture is used to knock polyatomic ions out of the path as

they collide with the cell gas. The ions are dissociated into their component atoms/ions or converted into non interfering species. The transmission of analyte ions is minimally affected. This process is called Kinetic Energy Displacement (KED). Most of the interferences from doubly charged ions have also been identified in literature. This type of interference cannot be circumvented but sometimes the effect can be slightly reduced through tuning. An example of this type is Ba++.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual, Lab Specific Addendum to the CSM, and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coat and closed-toe, nonabsorbent shoes are a minimum.

3.1 Specific Safety Concerns or Requirements

- The ICP-MS plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.
- Parts of the instrument can be extremely hot. Care should be taken if the instrument needs to be adjusted internally.
- Proper ventilation is required due to sample fumes and extreme heat generation (RF generator and plasma) and plasma emissions. People with medical conditions that may respond to ozone emissions should exercise caution.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material[1]	Hazards	Exposure Limit[2]	Signs and Symptoms of Exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Material[1]	Hazards	Exposure Limit[2]	Signs and Symptoms of Exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 EQUIPMENT AND SUPPLIES

- Argon gas: High purity grade (99.99%)
- Inductively Coupled Plasma Mass Spectrometer capable of providing resolution less than, or equal to, 0.9 AMU at 5% peak height from a mass range of at least 6-240 and a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass flow controller for the nebulizer argon and a peristaltic pump for the sample solution is recommended.
- A three channel peristaltic pump
- Appropriate water-cooling device
- Calibrated adjustable pipettes
- Autosampler with autosampler tubes
- Volumetric Flask (Class A): Varying volumes
- Helium
- Mass Hunter Workstation Software Patch 5

5.0 REAGENTS AND STANDARDS

5.1 Stock Standards

Stock standards are purchased as custom multi-element mixes or as single element solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock standard solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

5.2 Intermediate / Working Standards

5.2.1. Intermediate / Working standards are prepared as dilutions from the stock standards. Intermediate / working standard solutions are stored according to manufacturer's instructions. Intermediate / working standard solutions must be replaced after 6 months or according to the stock standard expiration date if less than 6 months. The intermediate / working standard solution must be replaced if verification from an independent source indicates a problem.

5.2.2. Refer to the LIMS standards and reagents module for further details on preparation of intermediate / working standard solutions.

5.3. Reagent water - ASTM Type I, or equivalent for the elements of interest, generated using an ion-exchange water polishing system.

5.4. Concentrated nitric acid (HNO_3), trace metal grade or better.

5.5. Concentrated hydrochloric acid (HCl), trace metal grade or better

6.0 Linear Range Standard/Interference Corrections

6.1 Linear Range Analysis Standard (LRS)

ICP/MS analysis involves a Linear Dynamic Range (LDR) and a Linear Calibration Range (LCR). At Eurofins Chicago, the high standard of the LCR is set below the established upper limit of the LDR for all elements. In order to establish, verify, and document linearity at or near that upper limit, a Linear Range Study (LRS) is done every six months on each instrument. This is done by running a single standard at the upper limit of the anticipated linear range of measurement after the instrument has been calibrated in the usual daily manner. The acceptance limits for these single-element verification standards is 90-110%. During routine analysis, all results, target or non-target, that are above the LDR are flagged by the instrument software, aiding the analyst in making appropriate dilution decisions. All samples for which a target analyte or an interfering element result is found to be above the LDR are diluted and re-analyzed until the concentration falls within 90% of the instrument's linear range.

6.2 Interference Corrections

Interference corrections are performed on known and observed interferences. These corrections are applied to the samples as needed and are documented with the ICP-MS raw data records and maintenance log records.

No Gas
Mc(51) = (M(51) * 1.0000) – (M(53) * 3.1270) + (M(52) * 0.3530)
Mc(75) = (M(75) * 1.0000) – (M(77) * 3.1270) + (M(82) * 2.5490)
Mc(98) = (M(98) * 1.0000) – (M(99) * 0.1460)
Mc(111) = (M(111)* 1.0000) – (M(108) * 1.0730) + (M(106) * 0.7640)
Mc(115) = (M(115)* 1.0000) – (M(118) * 0.0160)
Mc(208) = (M(208)* 1.0000) + (M(206) * 1.0000) + (M(207) * 1.0000)

Helium
Mc(44) = (M(44) * 1.0000) – (M(88) * 0.0153)
Mc(111) = (M(106)* 0.7640) – (M(108) * 1.0730) + (M(111) * 1.0000)
Mc(208) = (M(206)* 1.0000) + (M(207) * 1.0000) + (M(208) * 1.0000)

7.0 PROCEDURE

7.1 Quality Control Checks

The following section summarizes the quality control (QC) samples associated with ICPMS analysis.

QC Sample	Frequency	Control Limit [1]
Method Blank (MB)	1 per 20 samples	≤ Reporting Limit < MDL (Drinking Waters) ≤ ½ RL per QAPP
Lab Control Sample (LCS) [2]	1 per 20 samples	85 – 115 % (200.8) 80-120% (6020A/B)
Matrix Spike (MS) [3,6]	1 per 10 samples (200.8) 1 per 20 samples	70 – 130 % (200.8) 75-125% (80-120% per QAPP for 6020A/B)

		>50% (TCLP for 6020A/B)
Duplicates (MD) [4,6]	1 per 10 samples (200.8) 1 per 20 samples	20% RPD
Serial Dilution (SD)5x [5]	1 per 10 samples (200.8) 1 per 20 samples (6020A/B)	± 10% of the original result for 200.8/6020A ± 20% of the original result for 6020B
Post Digestion Spike (PDS) [7]	See below 1 per 20 samples (6020B)	75-125%

[1] Refer to Section 8 for additional details.
[2] LCS Duplicate (LCD) is performed only when required by the client or project.
[3] If sample concentration is ≤ 4X spike level, 70-130% (200.8) or 75-125% (6020A/B); if sample concentration is > 4X spike level, no control range. If TCLP matrix spike is < 50%, Standard Addition must be performed.
[4] If ≥ 5X reporting limit, 20% RPD; if < 5X reporting limit ± reporting limit; if < reporting limit no control range.
[5] If the analyte concentration is >100X the Reagent Blank, results should agree within ±10% of the original sample result.
[6]The sample selection for matrix QC, if not specified by the client or on the chain-of-custody, is rotated among client samples so that various matrix problems may be noted and/or addressed. Matrix spikes pre-determined by the digestion department.
[7] Post Digestion Spikes are analyzed on a project, program and client request basis. Method 6020A states that if the PDS is out, the sample should be diluted and re-run to overcome interferences.

7.2 Sample Preservation and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Holding Time [1]	Preservation[2]	Reference
Waters	180 days	HNO_3, pH < 2; Cool 4 ± 2°C	40 CFR Part 136.3

[1] Inclusive of digestion and analysis.
[2] Note: There is no regulatory requirement for keeping metals samples cold at 4 ± 2°C per chapter 3 table 3-2.

7.3 Sample Preparation

- The most commonly used digestion procedures for a water matrix are SW-846 Methods 3005A or EPA 200.8. Refer to UP-SP-3000 and UP-SP-200 for details on sample digestion.
- The turbidity is checked for all drinking water samples. If the turbidity is <1 NTU digestion is not required.
- All samples are checked for the proper preservation at time of sample receipt. If the samples were not preserved, they are acidified and held for at least 16 hours for method 200.8 or 24 hours for 6020 methods. A sticker is affixed to the sample bottles. The pH is rechecked prior to digestion following the waiting period, and if it is greater than 2 SU, more nitric acid is added and the sample is held an additional 16 or 24 hour minimum, the pH is documented in the digestion batch in the Initial pH column of the worksheet tab.

- The pH of the drinking water sample digestates are checked prior to prep / analysis. The documentation of this check will be recorded in the digestion batch in the Initial pH column on the worksheet tab. The lot# of the pH paper used is to be documented in the Batch Information screen of the AD batch.
- The pH of the non-digested drinking water samples are checked prior to analysis. The documentation of this check will be recorded in the soluble prep batch in the sample comment field. The lot# of the pH paper used is to be documented in the Batch Information screen of the AD batch.
- The samples are received in the metals laboratory at 25, 50 or 100 mL final volumes.

7.4 Calibration / Standardization

7.4.1 Instrument Set Up

The instrument is set up with the proper operating conditions as defined in the Thermo Electron and Agilent instrument manuals, using the recommended elements as outlined in the manual. The instrument must be allowed to become thermally stable (~15min to 30min.) prior to running a performance report and calibration.

The nebulizer pressure (see top bar of screen) should be approximately 1.8 – 2.5 bar. Higher nebulizer pressure is indicative of a clog in the nebulizer. The analyzer pressure should be 2.0-6.0 $X10^{-7}$ mbar. Lower analyzer pressure indicates the cones may require cleaning.

A tune is run once per week or additionally as needed to adjust the system for the best analysis. The tune can be done with an automated method, an auto tune, or done manually.

7.4.1.1 Tune Criteria (Performance Report)

A tune solution containing Cerium (Ce), Cobalt (Co), Lithium (Li), Magnesium (Mg), Thallium (Tl) and Yitrium (Y), at 1ug/L, is used. Initially a tune will attempt to maximize the count per second of each mass by adjusting the lenses and then the nebulizer.

He mode:

Mass	Counts	% RSD	Axis (Peak Error)	Width
Co59	>1500	< 5	58.9 - 60.1	0.65 - 0.85
Y89	>1500	< 5	88.9 - 89.1	0.65 - 0.85
Tl205	>1500	< 5	204.9 - 205.1	0.65 - 0.85

Ratio (Oxide): <2.0%

No gas mode:

Mass	Counts	% RSD	Axis (Peak Error)	Width
Li7	>1500	< 5	6.9 – 7.1	0.65 - 0.85
Y89	>4000	< 5	88.9 - 89.1	0.65 - 0.85
Tl205	>2000	< 5	204.9-205.1	0.65 - 0.85

Ratio (Oxide): <2.0%

Agilent P/A Factor: Can be run in warm-up sequence. Should be run at least 1x/week or when major hardware changes (such as cones) occur.
Mass Cal: Perform autotune when major hardware changes (such as, cones, nebulizer, torch) occur.

7.4.2 Standardization

Before any instrument is used as a measurement device, the instrument response to known reference materials must be determined. All sample measurements must be made within the linear range of the instrument. The instrument is standardized using a calibration blank and 5 calibration standards (Std1-5). The first calibration standard will be at the reporting limit. The calibration curve generated must have a correlation coefficient of $\geq$ 0.995 in order to consider the responses linear over that range. The high point of the curve for each element is verified prior to sample analysis. Results must be within 5% of the known concentration.

All samples found to be above the linear range are diluted and re-analyzed until the concentration falls within the instruments linear range. Sample analyte concentrations that are greater than 90% of the determined upper linear dynamic range (LDR) limit must be diluted and reanalyzed.

Standard	Frequency	Control Limit
Calibration Curve	Daily, initially	Corr. Coeff. ≥ 0.995 for 200.8, 6020B
High Standard (S1)	After the Calibration Curve	± 5% of the Known Conc.
Initial Cal. Verif. (ICV)	After the Calibration Curve	± 10% of the Known Conc.
Low-level ICV (ICVL) 6020A only - or MRL for DoD[1] 6020	ICVL after the Calibration Curve; MRL after ICB	± 30% of the Known Conc. (MRL ± 20% per QAPP[1]) ± 20% of the Known Conc. (6020B)
Initial. Cal. Blank (ICB)	After the ICV	≤ Reporting Limit (LLOQ) ≤ ½ RL per QAPP
CRI for 200.8	Daily, every 12hrs. thereafter	50-150%
ICSA / ICSAB[3]	Daily, every 12 hrs. thereafter (200.8) Daily (6020B)	± 20% of the Known Conc. (200.8).; ± 20% of the Known Conc. ; non-spiked < RL (< ½ RL per QAPP) (6020B)
Continuing Cal. Verif. (CCV)	Every 10 readings and end of each run	± 10% of the Known Conc.
Cont. Cal. Blank (CCB)	Every 10 readings; End of each run, after CCV/CCVL	≤ Reporting Limit (LLOQ) ≤ ½ RL per QAPP
Linear Range Verification Standard 6020B only	Daily[2]	± 10% of the Known Conc.

[1] Because there is no reporting limit standard in the calibration curve, an MRL is required for specific QAPPs/Programs, such as BP LaMP.
[2]Target and non-target interferences must be diluted below the level of the daily linear range standard. If the linear range verification standard is not run, the high standard in the calibration curve becomes the linear range.
[3] Method 6020B requires ICSA only.

7.4.3 5-point Calibration Curve

A 5 point calibration is prepared by diluting a custom standard of mixed analytes or individual stock standards to the following concentrations with acidified water. The highest standard in the calibration is used to meet the requirement of the LRC for 6020B.

Element	STD 1 (ppb)	STD 2 (ppb)	STD 3 (ppb)	STD 4 (ppb)	STD 5 (ppb)
Ag	0.5	1	10	20	100
Al	100	1000	10000	20000	50000
As	1	10	100	200	500
B	50	75	100	200	500

Ba	2.5	10	100	200	500
Be	1	10	100	200	500
Ca	200	1000	10000	20000	50000
Cd	0.5	10	100	200	500
Co	1	10	100	200	500
Cr	5	10	100	200	500
Cu	2	10	100	200	500
Fe	100	1000	10000	20000	50000
K	500	1000	10000	20000	50000
Li	10	50	100	200	500
Mg	200	1000	10000	20000	50000
Mn	2.5	10	100	200	500
Mo	4	10	100	200	500
Na	200	1000	10000	20000	50000
Ni	2	10	100	200	500
Pb	0.5	10	100	200	500
Sb	3	10	100	200	500
Se	2.5	10	100	200	500
Sn	5	10	100	200	500
Sr	4	10	100	200	500
Ti	5	10	100	200	500
Tl	2	10	100	200	500
V	5	10	100	200	500
Zn	20	50	100	200	500

7.5 Preventive Maintenance

The required preventive maintenance is listed in the maintenance logbooks which are kept at the instruments. All maintenance is recorded in these logbooks along with the date and the signature of the analyst performing the maintenance. The instruments are under a full service contract with the manufacturer for all major repairs.

7.5.1 Daily Maintenance

This includes monitoring the pump tubing for consistent sample uptake and a visible check of the waste container to make sure that it doesn't overflow. The pump tubing will be changed on an as needed basis.

7.5.2 Weekly Maintenance

This includes checking the tip of the torch, sampler, and skimmer cones for excessive buildup of material.

7.5.3 Monthly Maintenance

This includes cleaning and checking the water re-circulator for proper fluid level and cleaning the spray chamber.

7.6 Sample Analysis

7.6.1 Analytical Run

Before running any samples a performance report need to be run to verify that the instrument tune is still valid. If the performance report criteria and the 5 point calibration passes then sample

analysis can proceed. If the performance criteria are not met the instrument must be re-tuned. After retuning, the performance check is repeated. Once all performance criteria are met sample analysis can proceed.

After the instrument is standardized (Section 7.4.2), an analytical run is initiated. An example of the beginning of a run can be found in appendix 1.

The ICVL and CCVL are required for 6020A only. Reported data must be bracketed by these standards. The standards only need be run at the start and end of a run, but the analyst may choose to run them more frequently.

If the CCV and CCB results are acceptable, the run may continue without re-standardization. If any of the post-run QC is out of control, or close to being out of control, the instrument is re-standardized before analyzing the next batch. Any samples with elements associated with an out of control CCV or CCB will be reanalyzed.

An MRL may be required for methods 200.8 or 6020A and if so, is read at the frequency of 1 per batch at the beginning of the run, after the first CCB.

7.7 Documentation

7.7.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

7.7.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

7.7.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs are scanned and attached to the Documents section in the LIMS analytical batch.

7.7.4. Record all sample results and associated QC directly into LIMS. Level I and Level II reviews are performed in LIMS.

Examples of items included in the above reviews are as follows:

- QC data are outside the specified control limits for accuracy and precision
- Unusual detection limit changes are observed
- Samples having unusually high results
- Samples exceeding a known regulatory limit
- Raw data indicating some type of contamination or poor technique
- Transcription errors
- Results outside of calibration range

8.0 QUALITY CONTROL

8.1 QC Summary

NOTE: The following laboratory acceptance criteria are set at default control limits. Specific QAPPs may contain frequency or control limits that supersede those given here. Also, statistical limits are generated on an annual basis from cumulative LCS data and can be implemented when specified by the client, contract, or QAP.

8.1.1 Method Blank (MB)

At least one MB will be included in each digestion batch of 20 samples. Regardless of the matrix being processed, the MB will be in an aqueous media. The MBs are analyzed to determine if contaminants are being introduced into the sample via the sample preparation procedures.

8.1.2 Laboratory Control Sample (LCS)

At least one LCS will be included in each digestion batch of 20 samples. Regardless of the matrix being processed, the LCS will be in an aqueous media. The LCS is analyzed to determine the accuracy of the digestion process.

Accuracy will be measured by the percent recovery (%R) of the LCS. The recovery must be within ± 15% for 200.8 or 20% for 6020A/B of the known concentration. If the LCS results are outside these control limits, all samples in the preparation set must be redigested and reanalyzed. Refer to Table 6 for element concentrations.

8.1.3 Matrix Duplicate (DU)

A duplicate sample will be prepared at a frequency of 5% (1 in 20 samples). A 20% RPD is set as the acceptance limits.

8.1.4 Matrix Spike (MS)

The MS will be prepared at a frequency of 5% (1 in 20 samples). The recovery must be within 75–125% or 80-120% per QAPP. (Exception allowed if the sample concentration exceeds 4 times the spike added concentration.)

TCLP - If the MS recovery is <50% and the concentration does not exceed the regulatory limit or the sample concentration is within 20% of the regulation level, the Method of Standard Addition (MSA) is required. Three aliquots of the sample are spiked at 50%, 100% and 150% of the sample concentration or, if the sample concentration is < RL, the MSA is at 50%, 100% and 150% of the MS level. The data is subjected to linear regression whereas the concentration of the unknown is the x-intercept and the correlation coefficient (r) value must be $\geq$ 0.995.

Note: Either an MS/MSD or a DU/MS pair must be prepared at a frequency of 5% (1 in 20 samples).

8.1.5 Serial Dilution

A Serial Dilution (5X) will be prepared from the digestate at a frequency of 5% (1 in 20 samples). If the concentration is >25 times the LLOQ (RL), results should agree within +/- 20% of the original results.

8.1.6 Post Digestion Spike

If the MS/MSD is not within limits a Post Digestion spike must be analyzed for the failed analytes. The test only needs to be performed for the specific elements that failed the original MS limits. If the PDS is out, the sample results must be reported as estimated values. Recovery limits must be between 75-125%

8.2 Corrective Action

When an out-of-control situation occurs, the analysts must use his/her best analytical judgment and available resources to determine the corrective action to be taken. The out- of-control situation may be caused by more than one variable. The analyst should seek the assistance of his/her supervisor, QA personnel, or other experienced staff if he/she are uncertain of the cause of the out-of-control situation. The analysis must not be resumed until the source of the problem and an in-

control status is attained. All samples associated with the out-of-control situation should be reanalyzed. Out-of-control data must never be released without approval of the supervisor, or QA personnel.

The following steps that must be taken when an out-of-control situation occurs:

- demonstrate that all the problems creating the out-of-control situation were addressed;
- document the problem and the action which was taken to correct the problem on an NCM;
- document on the NCM that an in-control has been achieved; and
- receive approval (signature) of the supervisor or QA personnel prior to the release of any analytical data associated with the problem.

QC Indicator	Suggested Corrective Actions
Calibration Curve	• reanalyze the standard curve; • prepare a new stock and/or working standards; • check the reagents/solutions and prepare fresh if necessary.
ICV	• repeat the ICV to verify proper preparation; • prepare a new ICV from original stock; • recalibrate with a new standard curve; • prepare a new stock and/or working standards; • check the reagents/solutions and prepare fresh if necessary.
ICVL	• repeat the ICVL to verify proper preparation; • prepare a new ICVL from original stock; • recalibrate with a new standard curve; • prepare a new stock and/or working standards; • check the reagents/solutions and prepare fresh if necessary.
ICB	• prepare a new ICB to verify proper preparation; • verify that the instrument base-line is stable and perform necessary maintenance, cleaning, etc.. to achieve stability; • determine the source of contamination by process of elimination, carryover from a previous analysis or reagent contamination and correct the problem; • check the reagents/solutions and prepare fresh if necessary; • correct for any contamination and reanalyze the ICB and any associated samples.
LCS	If the LCS is low: • reanalyze the LCS and all samples in the set for the failed analyte(s) to confirm that it is out of control. • If continued out of control, redigest and reanalyze the set. • Write an NCM. If the LCS is high: • reanalyze the LCS and all samples in the set for the failed analyte(s) to confirm that it is out of control. • check for contamination of reagents, LCS stock solution, or in the preparation area; • correct for contamination, redigest and re-analyze the set; • Write an NCM.

QC Indicator	Suggested Corrective Actions
MB	• reanalyze the MB to verify that it is beyond the LLOQ (RL); • determine the source of contamination; • determine if a high value is due to contamination; • check for contamination of reagents or in the preparation area; • correct for contamination, reanalyze the set; • in the extreme case where all samples in the set are at least 10x > the MB or < LLOQ (RL), reanalysis will not be required; however, an NCM will be written and approved by the supervisor or section manager.
DU	• an NCM will be written and approved by the supervisor or section manager per client request.
MS	• an NCM will be written and approved by the supervisor or section manager per client request.
Serial Dilution (SD)	• prepare a new serial dilution to verify proper preparation; • an NCM will be written and approved by the supervisor or section manager per client request.
Post Digestion Spike (PDS)	• Flag and report data as estimated values
CCV	• repeat the CCV to verify proper preparation; • prepare a new CCV from the original stock; • check for instrument base-line drift or a change in one or more of the reagents; • check the reagents/solutions and prepare fresh if necessary; • recalibrate with a new standard curve and repeat all samples since the previous in control CCV; • never dispose of any samples until you are sure that all QC are within the control limits.
CCB	• check reagents/solutions to verify proper preparation and prepare fresh if necessary; • verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc., to achieve stability; • correct for any contamination (carryover from a previous analysis or reagent contamination) and reanalyze the CCB and any associated samples; • never dispose of any samples until you are sure that all QC are within the control limits.
Linear Range Check	Target and non-target interferences must be diluted below the level of the daily linear range standard. If the linear range verification standard is not run, the high standard in the calibration curve becomes the linear range.
Additional CAs	• If any of the ICV, ICB, ISA, CCV or CCB results is out-of-control for any element, the instrument is restandardized and the samples associated with the out-of-control elements are reanalyzed. • If the MB or LCS is out of control for any element, the samples are redigested. An exception is if the sample concentrations are ≥ 10X the MB contamination or < LLOQ (RL). In this case, the results are reported as is. • If any of the DU or MS results are out of control, the client is notified of the poor results via a case narrative that is sent with the data report. • NCMs are completed by the analyst performing the analysis then reviewed and signed by the supervisor or section manager.

9.0 DATA ANALYSIS AND CALCULATIONS

The sample results are stored in a data file on the desktop computer. The data file is transferred directly to TALS. This system helps to eliminate transcription errors, since data is not entered by hand.

9.1 Accuracy

9.1.1 ICV / CCV, LCS % Recovery

$$\frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

9.1.2 MS % Recovery

$$\frac{(\text{spiked sample}) - (\text{unspiked sample})}{\text{spike concentration}} \times 100$$

9.2 Precision (RPD)

9.2.1 Matrix Duplicate (MD)

$$\frac{|\text{orig. sample value} - \text{dup. sample value}|}{[\frac{\text{orig. sample value} + \text{dup. sample value}}{2}]} \times 100$$

9.3 Concentration

$$\frac{\text{mg}}{\text{KG}} \text{ or } \text{L} = \frac{\text{C} \times \text{V} \times \text{D}}{\text{W}}$$

Where:
C = sample concentration in extract (ppm)
V = Volume of extract (mL)
D = Dilution Factor
W = Volume of sample aliquot extracted (mL)
NOTE: All dry weight corrections are made in LIMS at the time the results are processed in the analytical batch.

9.4 Calculations for Hardness

All expressed as calcium carbonate.

Calculation of Magnesium Hardness

(Mg) Magnesium Raw (mg/L) * 4.118 * PF

Calculation of Calcium Hardness

(Ca) Calcium Raw (mg/L) * 2.497 * PF

Calculation of Total Hardness

[((Ca) Calcium Raw (mg/L) * 2.497) + ((Mg) Magnesium Raw (mg/L) * 4.118)] * PF

Final units appropriate to reporting requirements.

PF=Prep Factor

Note: All the raw data associated with the calculation of the Total Hardness results resides within the ICPMS analytical batch where the Ca and Mg results are analyzed for each sample. All QC associated with the Ca and Mg are calculated, evaluated and must meet acceptance criteria before the Total Hardness results can be calculated and reported. The Total Hardness method in TALs is a calculation method only that imports the Ca and Mg final results obtained from the 200.8 analytical batch and performs the calculation.

10.0 POLLUTION CONTROL

It is Eurofins policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

10.1 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to UP-WM-001.

The following waste streams are produced when this method is carried out.

- Waste from this procedure will enter the "Corrosive Wastewater" wastestream.

11.0 METHOD PERFORMANCE CRITERIA

Refer to Sections 1.0, 7.0 and 8.0.

12.0 REFERENCES

Refer to Section 1.0.

13.0 ATTACHMENTS

Table 1 Element and Reporting Limits
Table 2 Calibration Standard Concentrations and Stocks
Table 3 ICV Concentrations and Stocks
Table 4 CRI Concentrations and Stock
Table 5 ICSA / ISCAB Concentrations and Stocks
Table 6 Known Digested Quality Control
Table 7 Internal Standard (IS) Application

Attachment 1 Example: Maintenance Log

Appendix 1 Example of beginning of run

14.0 REVISION HISTORY

- Revision 0
- Combined SOPs UME-2008. UME-6020 and UME-6020B

Table 1
Element and Reporting Limits

Element	ICP-MS Isotopes (AMU)	Reporting Limits [1] Waters (ug/L)
Al	27	100
Sb	121	3.0
As	75	1.0
Ba	137	2.5
Be	9	1.0
B	11	50
Ca	44	200
Cd	111	0.5
Cr	52	5.0
Co	59	1.0
Cu	63	2.0
Fe	54	100
Pb	208	0.5
Li	7	10
Mg	24	200
Mn	55	2.5
Mo	95	4.0
Ni	60	2.0
K	39	500
Se	78	2.5
Ag	107	0.5
Na	23	200
Sr	88	4.0
Tl	205	2.0
Sn	118	5.0
Ti	47	5.0
V	51	5.0
Zn	66	20
Li^2	6	N/A
Sc^2	45	N/A
Y^2	89	N/A
In^2	115	N/A
Rh^2	103	N/A
Tb^2	159	N/A
Bi^2	208	N/A
Ge	72	N/A
Ir	193	N/A

[1] These are routine ICPMS reporting limits (RLs). RLs will vary depending on sample size/volume, dilution factors, and changes in MDLs.
[2] Used as an internal standard and is introduced continuously to all samples (including standards and QC samples) via the peristaltic pump. See section 5.2.1 for concentrations.

Table 2
Calibration Standards and CCV Concentrations and Stocks mg/L

Vendor/Stock ID & Concentration	Element	Std2	Std3	Std4	Std5	CCV
Inorganic Ventures STLIL-STD-2 100 mg/L	Sb	0.01	0.1	0.2	0.5	0.25
	Mo	0.01	0.1	0.2	0.5	0.25
	Sn	0.01	0.1	0.2	0.5	0.25
	Ti	0.01	0.1	0.2	0.5	0.25
CPI Single Element, 10 mg/L	Ag	0.001	0.01	0.02	0.1	0.05
Inorganic Ventures STLIL-STD-1 100 mg/L	As	0.01	0.1	0.2	0.5	0.25
	Ba	0.01	0.1	0.2	0.5	0.25
	Be	0.01	0.1	0.2	0.5	0.25
	B	0.01	0.1	0.2	0.5	0.25
	Cd	0.01	0.1	0.2	0.5	0.25
	Co	0.01	0.1	0.2	0.5	0.25
	Cr	0.01	0.1	0.2	0.5	0.25
	Cu	0.01	0.1	0.2	0.5	0.25
	Mn	0.01	0.1	0.2	0.5	0.25
	Pb	0.01	0.1	0.2	0.5	0.25
	Ni	0.01	0.1	0.2	0.5	0.25
	Se	0.01	0.1	0.2	0.5	0.25
	Sr	0.01	0.1	0.2	0.5	0.25
	Tl	0.01	0.1	0.2	0.5	0.25
	V	0.01	0.1	0.2	0.5	0.25
	Zn	0.01	0.1	0.2	0.5	0.25
Inorganic Ventures RFW-ICPT-STD-2A 10,000 mg/L	Al	1	10	20	50	25
	K	1	10	20	50	25
Inorganic Ventures RFW-ICPT-STD-2B 5,000 mg/L	Ca	1	10	20	50	25
	Fe	1	10	20	50	25
	Mg	1	10	20	50	25
	Na	1	10	20	50	25
CPI Single Element, 100 mg/L	Li	0.05	0.1	0.2	0.5	0.25
CPI Boron 100 mg/L	B	0.065	0.0	0.0	0.0	0.00
CPI Zinc 100 mg/L	Zn	0.04	0.0	0.0	0.0	0.00

Note: 6020A states that the lowest point of a multipoint calibration curve should be at the RL. Eurofins Chicago runs the MRL and/or low-level ICV/CCV as verification at this level.

Table 3
ICV Concentrations and Stocks

Vendor Stock Name	Element	ICV (mg/L)
High Purity SM-606-107 100 mg/L	As	0.20
	Ba	0.20
	Be	0.20
	B	0.20
	Cd	0.20
	Co	0.20
	Cr	0.20
	Cu	0.20
	Mn	0.20
	Ni	0.20
	Pb	0.20
	Se	0.20
	Sr	0.20
	Tl	0.20
	V	0.20
	Zn	0.20
	Mo	0.20
	Sb	0.20
	Sn	0.20
	Ti	0.20
High Purity SM-606-108 10,000 mg/L	Al	20
	K	20
	Ca	20
	Fe	20
	Mg	20
	Na	20
CPI G34-4400-10511-100SS 10 mg/L	Ag	0.04
CPI G34-4400-100PM291-100 SS 100mg/L	Li	0.20

[1] This is used for 6020A, and 6020B only

Table 4
MRL / ICVL / CCVL Concentrations and Stock

Element	TACHI-STD-1 (mg/L)	STD-1 (mg/L)
Al	100	0.100
Sb	3	0.003
As	1	0.001
Ba	2.5	0.0025
Be	1	0.001
B	50	0.050
Ca	200	0.200
Cd	0.5	0.0005
Cr	5	0.005
Co	1	0.001
Cu	2	0.002
Fe	100	0.100
Pb	0.5	0.0005
Li	10	0.010
Mg	200	0.200
Mn	2.5	0.0025
Mo	4	0.004
Ni	2	0.002
K	500	0.500
Se	2.5	0.0025
Ag	0.5	0.005
Na	200	0.200
Sr	4	0.004
Tl	2	0.002
Sn	5	0.005
Ti	5	0.005
V	5	0.005
Zn	20	0.020

Table 5: ICSA / ISCAB Concentrations and Stocks

Vendor / Stock ID	Element	Stock Conc. (mg/L)	ICSA Conc. (mg/L)
CPI TA-ICPMS-ICSA	Cl	10,000	1000
	C	2,000	200
	Al	1,000	100
	Ca	1,000	100
	Fe	1,000	100
	K	1,000	100
	Mg	1,000	100
	Na	1,000	100
	P	1,000	100
	S	1,000	100
	Mo	20	2
	Ti	20	2
			ICSAB Conc. (mg/L)
CPI TA-ICPMS-ICSA	Cl	10,000	1000
	C	2,000	200
	Al	1,000	100
	Ca	1,000	100
	Fe	1,000	100
	K	1,000	100
	Mg	1,000	100
	Na	1,000	100
	P	1,000	100
	S	1,000	100
	Mo	20	2
	Ti	20	2
CPI TA-ICPMS-ICSAB	Ag	2	0.02
	As	2	0.02
	Cd	2	0.02
	Co	2	0.02
	Cr	2	0.02
	Cu	2	0.02
	Mn	2	0.02
	Ni	2	0.02
	Zn	2	0.02
	B-	5	0.05
	Ba	2	0.02
	Be	2	0.02
	Pb	2	0.02
	Sb	2	0.01
	Se	2	0.02
	Sr	2	0.02
	Tl	2	0.01
	V	2	0.02
	Li	2	0.02

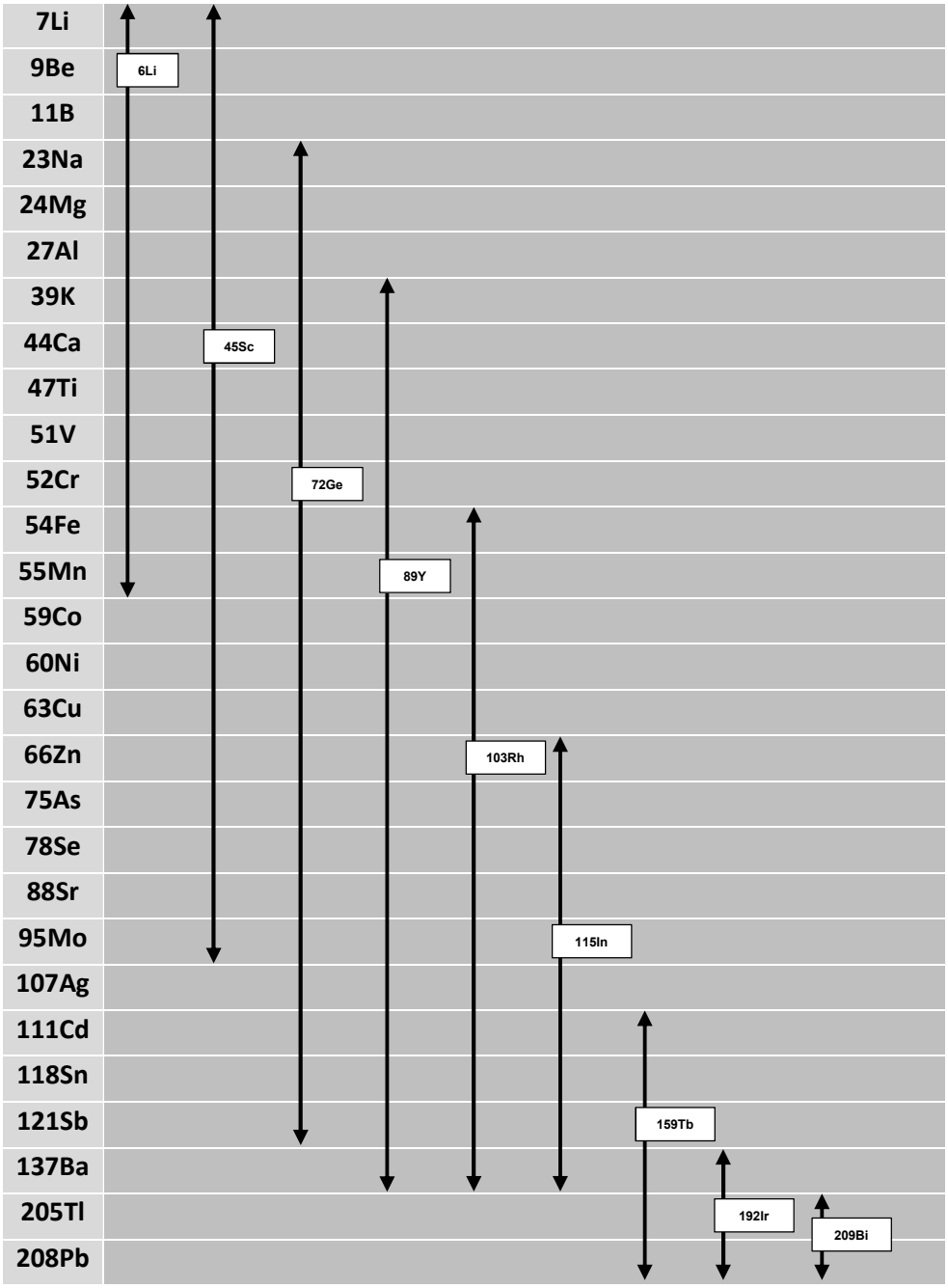
Table 6
Known Digested QC Values (mg/L)

Element	LCS/Spike
27Al	2
121Sb	0.5
75As	0.1
137Ba	0.5
9Be	0.05
11B	1
111Cd	0.05
44Ca	10
52Cr	0.2
59Co	0.5
63Cu	0.25
54Fe	1
208Pb	0.10
24Mg	10
55Mn	0.5
95Mo	1
60Ni	0.5
7Li	0.10
39K	10
78Se	0.10
107Ag	0.05
23Na	10
88Sr	1
205Tl	0.10
118Sn	1
47Ti	1
51V	0.5
66Zn	0.5

Default Control Limits-200.8
LCS: 85 - 115%
Spike: 70- 130%

Default Control Limits- 6020A, and 6020B
LCS: 80 - 120%
Spike: 75 - 125%
TCLP Spike: >50%

Table 7
ICP/MS Internal Standard (IS) Application



Note: Data may be evaluated against any IS within the 50 AMU range as represented by the arrows above. An alternate IS may be used due to a natural overabundance of an IS standard in the sample or due to a spiked solution used in the sample that contains the IS in question. The selected IS will be used for the entire analysis run.

Appendix 1
Example of beginning of run

Before running any samples a performance report needs to be run to verify that the instrument tune is still valid. If the performance report criteria and the 5 point calibration passes then sample analysis can proceed. If the performance criteria are not met the instrument must be re-tuned. After retuning, the performance check is repeated. Once all performance criteria are met sample analysis can proceed.

Method 200.8:

- S1 Reanalysis of calibration standard as a sample
- ICV Initial Calibration Verification
- ICB Initial Calibration Blank
- ICSA Interferent Check Standard A
- ICSB Interferent Check Standard B
- CCV Continuing Calibration Verification
- CCB Continuing Calibration Blank
- MB (1) Method Blank
- LCS (2) Laboratory Control Sample
- Sample (3) Sample
- Sample (4) Serial Dilution (L)
- Sample (5) Matrix Duplicate (MD)
- Sample (6) Matrix Spike (MS)
- Sample (7)
- Sample (8)
- Sample (9)
- Sample (10)
- CCV Continuing Calibration Verification
- CCB Continuing Calibration Blank

Method 6020A:

- S1 Reanalysis of calibration standard as a sample
- ICV Initial Calibration Verification
- ICVL Low-level ICV (6020A only)
- ICB Initial Calibration Blank
- CRI Spiked Blank Sample
- ICSA Interferent Check Standard A
- ICSB Interferent Check Standard B
- CCV Continuing Calibration Verification
- CCB Continuing Calibration Blank
- MB (1) Method Blank
- LCS (2) Laboratory Control Sample
- Sample (3) Sample
- Sample (4) Serial Dilution (L)
- Sample (5) Matrix Duplicate (MD)
- Sample (6) Matrix Spike (MS)
- Sample (7) Matrix Spike Duplicate (MSD)
- Sample (8) Post Digestion Spike (PDS)
- Sample (9)
- Sample (10)
- CCV Continuing Calibration Verification
- CCVL Low-level CCV (6020A only)
- CCB Continuing Calibration Blank

The ICVL and CCVL are required for 6020A only. Reported data must be bracketed by these standards. The standards only need be run at the start and end of a run, but the analyst may choose to run them more frequently.

Method 6020B:

- S1 Reanalysis of calibration standard as a sample
- ICV Initial Calibration Verification
- ICVL Low-level ICV
- ICB Initial Calibration Blank
- CRI Spiked Blank Sample
- ICSA Interferent Check Standard A
- CCV Continuing Calibration Verification
- CCB Continuing Calibration Blank
- MB (1) Method Blank
- LCS (2) Laboratory Control Sample
- Sample (3) Sample
- Sample (4) Serial Dilution (SD)
- Sample (5) Post Digestion Spike (PDS)
- Sample (6) Matrix Duplicate (MD)
- Sample (7) Matrix Spike (MS)
- Sample (8)
- Sample (9)
- Sample (10)
- CCV Continuing Calibration Verification
- CCB Continuing Calibration Blank
- LRC Linear Range Check Standard

Eurofins Chicago

STANDARD OPERATING PRACTICE (SOP) CHANGE FORM

Original SOP Number/Revision #: UP-SP-3000, Rev. 35 Last Mod ID (circle): NA/ _____

SOP Title: Metals Digestion by SW-846 3000 Series

Affected SOP Section Number(s): See below
Effective Date of Change: 4/23/24

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Full Signature Approvals Are Kept on File with Eurofins Chicago Standard Practice Records

Revision Number with Mod ID:

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. **Append this form to the front of the SOP copy.**

1. Reason for SOP Change:
There were a few sections that were missed when removing the requirement of filtering non-dissolved samples.

2. Summary of Procedure Change (circle to indicate if there are attachments t this form: No / Yes: # pages attached = ___)
Section 7.6.1, 7.6.1.1 and 7.6.3: Filtering is optional for non-dissolved samples. There is a typo in section 7.6.1.

4/23/24
Initiated/Reviewed By: Name/Date

Julie Johnson 4/23/24
Approval Signature/Date: Section Manager

Initiated/Reviewed By: Name/Date

4/23/24
Approval Signature/Date: QA Manager or Designee

TITLE: SAMPLE PREPARATION
Metals Digestion by SW-846 3000 Series

Approvals (Signature/Date):

Debbie Johnson 2/15/24
Debbie Johnson Date
Supervisor, Metals Dept.

Chris Hoham 2/15/24
Chris Hoham Date
Env. Health & Safety Coordinator

Nicole Berg 2/15/24
Nicole Berg Date
Quality Assurance Manager

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1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) outlines the guidelines for the preparation of wastewaters, extracts, wastes and soil samples for metals analysis by Trace Inductively Couples Argon Plasma (ICP) and Inductively Coupled Argon Plasma / Mass Spectrometry (ICP-MS). This SOP was written using the following methods of SW-846, Third Edition:

Method	Description
3005A	Surface and ground waters for analysis by Trace ICP, ICP-MS
3010A	Waters and extracts for analysis by Trace ICP
3030C	See note below.
3050B	Soil and waste samples for analysis by Trace ICP

On occasion, clients request slight modifications to this SOP. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP), authorized via laboratory signature approval, and mentioned in the data package's case narrative.

Note: The state of North Carolina requires the use of Standard Methods 3030C for the preparation of wastewater samples.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

Not Applicable. Refer to the analytical SOPs.

1.1.2 Reporting Limits

Not Applicable. Refer to the analytical SOPs.

1.1.3 Definitions

Refer to Section 3.0 of the Laboratory's Quality Assurance Manual (UP-QA_QAM).

1.2 Summary of Method

Water and soil samples are digested with nitric acid, hydrochloric acid and/or hydrogen peroxide to produce digestates that are in the correct acid media for analysis by the Trace ICP or ICP-MS.

2.0 INTERFERENCES

Matrix interferences are usually not present for the digestion process. Analytical matrix interferences may be apparent during the instrumental analysis of the digestates. The types of interferences for the instruments are discussed in the appropriate SOPs.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual, Lab Specific Addendum to the CSM, and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coat and closed-toe, nonabsorbent shoes are a minimum.

3.1 Specific Safety Concerns or Requirements

- Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.
- Acid vapor can be dangerous. Work in a well ventilated area (i.e., fume hood).
- Hydrogen peroxide (H_2O_2) is a strong oxidizer and is corrosive. The digestion must be cooled sufficiently before the addition of H_2O_2 to avoid a reaction and possible violent effervescence, or boiling over of the digestion. A splash/splatter hazard is possible and a face shield should be worn

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE:** This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material [1]	Hazards	Exposure Limit [2]	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrogen Peroxide	Oxidizer Corrosive	1 ppm-TWA	Vapors are corrosive and irritating to the respiratory tract. Vapors are very corrosive and irritating to the eyes and skin.

Material [1]	Hazards	Exposure Limit [2]	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

[1] – Always add acid to water to prevent violent reactions.
[2] – Exposure limit refers to the OSHA regulatory exposure limit.

4.0 EQUIPMENT AND SUPPLIES

- Top loading balance
- Hot plate (w/ thermometer)
- Hot Block w/ digestion vessels (w/ thermometer)
- 250 mL beakers
- 100 mL graduated cylinders
- Whatman No. 541 filter paper
- Funnels
- Fume hood(s)
- Eppendorf Pipettes
- Watch glasses (ribbed & non-ribbed)
- Filters and plunger apparatus[1]
- 100 & 50 mL digestate vessels[1] (which are checked to ensure volume markings at 25 mL, 50 mL, and 100 mL are within 2.5% Tolerance).
- 100 mL Snap-Cap containers for digestates (which are checked to ensure volume markings are within 2.5% Tolerance).
- Teflon strips (soils)
- pH Paper

[1]Each time the metals digestions staff opens a new case/box of filters or digestion tubes, the certificate must be removed and the lot number compared with previous lot numbers. If the case/box has a new lot number, the filters or digestion tubes must be verified as free of metals contamination to the lowest reporting level by in-house testing. This will be accomplished as follows:

1. Prep analyst identifies new lot and documents the prep batch number for the first ICP and ICPMS MB created on the vendor supplied quality certificate.
2. The lot number will be documented in the comments section of the LIMs prep batch.
3. The certificate will be forwarded to the instrument analyst attached to the metals digestion sheet.
4. After the analysis of the MB, the raw data will be reviewed to determine if the acceptance criteria of results falling below ½ the current RL are met.

5. If the acceptance criteria are met, the analyst or supervisor will initial and date the certificate to indicate approval and document the analysis run and batch where the results may be found.
6. If the criteria are not met, the analyst must notify their supervisor immediately who will then initiate corrective action measures.
7. The certificate will be maintained on file in the Metals Department.

Note: Any consumable items for which a lot number is required to be tracked, must be stored with the lot number present. **Do Not** Separate the containers (boxes/bags) with the lot number identified from the consumable item until that consumable item is all used up.

5.0 REAGENTS AND STANDARDS

5.1 Reagents

- Concentrated Nitric Acid
- Concentrated Hydrochloric Acid
- 30% Hydrogen Peroxide Solution
- 30% Ultrex II Ultra Pure Hydrogen Peroxide Solution

Purchased from a chemical vendor.

- Life of Reagent: Specified by the Manufacturer, concentrated acids 5 years
- Storage Requirements: Acid Cabinet

5.2 Standards

5.2.1 ICP and ICP-MS Intermediate Standards

These standards are prepared from multi-element solutions purchased from vendors. Single element stocks are also required. These purchased solutions expire 1-year from the date of receipt.

Standard	Preparation
ICP Spike Solution And ICP-MS Spike Solution	**For both ICP and ICPMS**, add ~400 mL of Milli-Q water to a 1-L Class A volumetric flask. **For ICP**, add 100 mL each of HP1381-A-500, HP1381-B-500 and HP1381-C-500 **For ICPMS**, add 100 mL each of HP2930-A-500, HP2930-B-500, HP2930-C-500 **For both ICP and ICPMS**, add the following: • 9 mL of 1,000 ppm Se; • 8 mL of 1,000 ppm Pb; • 6 mL of 1,000 ppm As; • 5 mL of 1,000 ppm Tl; and • 40 mL of InstraPure nitric acid.

	Swirl to mix; Dilute to volume with Milli-Q water. Life of Standard: Expiration date of the earliest expiring standard. Storage Requirements: None.

6.0 CALIBRATION (NON-DAILY)

Not Applicable.

7.0 PROCEDURE

7.1 Quality Control Checks

QC Indicator	Preparation	Frequency
Method Blank (MB)	For soil sample batches, use 5 – 10 mL of Milli-Q water. [1]	1 per 20 or fewer samples.
	For water sample batches, use 50 mL of Milli-Q water.	1 per 20 or fewer samples.
Matrix Duplicate (DU) [2]	Aliquot of the same field sample that is digested independently.	1 per 20 or fewer samples.
Laboratory Control Sample (LCS) [3]	For soil sample batches, use a Teflon strip, 5 – 10 mL of Milli-Q water and spike as listed below. [1, 4]	1 per 20 or fewer samples.
	For water sample batches, use 50 mL of Milli-Q water and spike as listed below. [4]	1 per 20 or fewer samples.
Matrix Spike (MS); MS Duplicate (MSD) [2]	Aliquot of the same field sample that is spiked as listed below [4] and digested independently.	1 per 20 or fewer samples.

[1] The use of a 'soil' matrix for the preparation of Soil MB's and LCS's, Teflon Strands or another inert material will be incorporated. The lot number of the inert material will be documented in the preparation batch notes.
[2] The sample selection for MS/MSD/DU is rotated among client samples so that various matrix problems may be noted and/or addressed.
[3] LCS Duplicate (LCSD) is performed when requested by the client, contract or QAP.
[4] The LCS and MS/MSD are spiked with a known amount of analyte and processed through the digestion procedure. The spiking procedure is as follows:

Instrument	Waters Spike Volume	Soils Spike Volume
ICP or ICP-MS	0.5 mL of ICP or ICP-MS Intermediate Spiking Solution.	1 mL of ICP or ICP-MS Intermediate Spiking Solution.

Refer to Appendix A for the individual element concentrations within the spiking solutions. . Matrix spikes for TCLP extracts are added after filtration of the TCLP extract and before preservation. Refer to SOP No. UP-SP-1311.

- **Matrix spikes for solid matrices are to be spiked prior to adding the water.**
- **Matrix spikes for TCLP extracts are added after filtration of the TCLP extract and before preservation. Refer to UP-SP-1311.**

7.2 Sample Preservation and Storage

Matrix	Holding Time	Preservation
Waters	180 days	HNO_3, pH <2; Cool 4 ± 2°C
Soils	180 days	Cool 4 ± 2°C

Note: If the metals water samples are not preserved, they will be preserved in login and a sticker will be placed over the lid of the sample bottle. This pre-printed sticker will document "Sample preserved in login, do not analyze for 24 hours".

7.2.1 Sample Handling Procedures (Other than Soils / Waters)

Matrix	Description
Wipes	The entire wipe is digested with results reported as ug/wipe.
Paint Chips	Care is taken to remove the paint from the substrate. The chips are then cut and ground to provide a uniform matrix from which to take a sample aliquot. Sample size is approximately 1.0 grams.
Solids *	Dried and ground with a mechanical crusher.

*Bricks, wood, etc.

7.3 Sample Preparation

- Since the pH is checked by the sample custodian at sample receipt, the digestion analyst will check the pH at random if the analyst has a reason to suspect that the sample may not be preserved.
- The start temperature of the hot plate or hot block digestion is documented in the TALS prep batch. The thermometer must be rotated in the hot block with each digestion batch, documenting the Position in the TALs prep batch.

7.3.1 Sample Preparation (Dissolved)

Samples that are to be reported as "Dissolved" which have **NOT** been filtered in the field, are logged with a "Filtration" pre-Prep in TALs and will be filtered in the laboratory, ideally within 48 hours of sample receipt.

The filtration procedure is as follows:

1. An unpreserved sample aliquot of approximately 250 mL is pressure filtered through a 0.45 um filter into a 250 ml plastic sample bottle. (Document Filter Lot # in the filtration batch in TALs)
2. For metals analysis the filtrate is preserved with HNO3 to pH < 2. (Document Acid Lot # in filtration batch in TALs)
3. For metals analysis a sticker is placed on the filtrate stating "Do not analyze for 24 hours".
4. Each sample filtrate is issued a unique sample ID TALs label ensuring that the sample is traceable to the filtration batch.
5. The filtration apparatus is cleaned after each use.

NOTE: The LCS and MB must be filtered through the 0.45 um filter prior to being analyzed with samples logged for dissolved metals.

7.4 Calibration / Standardization

Not Applicable.

7.5 Preventive Maintenance

- To minimize contamination during sample preparation, the fume hoods and counter areas must be kept clean and free of dust.
- The digestion hoods are cleaned on a regular basis (a minimum of once a month) and documented within the hood maintenance log.

7.6 Sample Digestion

7.6.1 Method 3005A

- Transfer 50 mL of the well-mixed (homogenized) sample into a 50 mL digestion vessel.
- Add 1 mL of concentrated nitric acid and 2.5 mL of concentrated hydrochloric acid.
- Cover the vessel with a ribbed watch glass and heat on a preheated hot block at 90-95˚C until the volume has been reduced to ~10 mL. Do not allow the samples to boil.
- Remove the vessels from the hot block and allow to cool.
- Fill to a 50 mL final volume in the digestion vessel with Milli-Q water; sample be be filtered by using the plunger apparatus.
- The sample is now ready for analysis.

NOTE: When using the Hot Plates, all volumes remain the same in the 250 mL beaker. Transfer the digestate to a digestion vessel, washing down the sides of the beaker with Milli-Q water as needed. Dilute the sample to a 50 mL final volume using Milli-Q water and filter using the plunger apparatus.

7.6.1.1 Method 3005A-Modified for ICP-MS

- Transfer 50 mL of the well-mixed (homogenized) sample into a 50 mL digestion vessel.
- Add 1 mL of concentrated nitric acid and ***0.5 mL**** of concentrated hydrochloric acid.
- Cover the vessel with a ribbed watch glass and heat on a preheated hot block at 90-95°C until the volume has been reduced to ~10 mL.
- Remove the vessels from the hot block and allow to cool.
- Fill to a 50 mL final volume in the digestion vessel with Milli-Q water; samples may be filtered by using the plunger apparatus.
- The sample is now ready for analysis.

***NOTE:** Method 3005A was modified for ICP-MS to matrix match the preparation with the analytical standards. In this regard, a volume of 0.5 mL of concentrated hydrochloric acid is added to the digestion vessel in place of 2.5 mL. Hydrochloric acid is a known interferent on the ICP-MS.

7.6.2 Method 3010A

Used for aqueous samples and extracts for ICP analysis.

- Transfer 50 mL of the well-mixed (homogenized) sample into a 50 mL digestion vessel.
- Add 1.5 mL of concentrated nitric acid.
- Cover the vessel with a ribbed watch glass and place on a preheated hot block set at 90-95°C.
- Evaporate the sample down to a low volume (approximately 5 mL) – just enough to cover the bottom of the vessel. **The sample should not boil or evaporate completely on any portion of the bottom of the vessel. If this should happen, a re-digestion must be done.**
- Remove the vessel from the hot block and allow to cool for 20 minutes
- Add another 1.5 mL portion of concentrated nitric acid.
- Cover the vessel with a non-ribbed watch glass and return to the hot block to allow a gentle reflux to occur.
- Continue to add concentrated nitric acid as necessary, until the digestion is complete (no change in appearance with continued refluxing).
- Uncover and evaporate to a low volume, not allowing any part of the vessel to go dry.
- Remove the vessels from the hot block and allow to cool for 20 minutes
- Add 2.5 mL of concentrated hydrochloric acid.
- Warm the vessel for another 15 minutes to dissolve any precipitate.
- Remove from hot block and allow to cool for 20 minutes.
- Fill to a 50 mL final volume in the digestion vessel with Milli-Q water and filter using plunger apparatus. Alternatively, if samples are allowed to settle, filtering may not be required.
- The sample is now ready for analysis.

NOTE: When using the Hot Plate, the volume remains the same in a 250 mL beaker. Transfer the digestate to a digestion vessel, washing down the sides of the beaker with Milli-Q water as needed. Dilute the sample to a 50 mL final volume using Milli-Q water and filter using the plunger apparatus.

7.6.3 Method 3030C

- Transfer 50 mL of well mixed (homogenized) sample into a digestion vessel.
- Add 1.25 mL of concentrated hydrochloric acid.
- Heat 15 minutes on hot block, at 90-95 degrees C.
- Remove from hot block and allow to cool for 20 minutes.
- Filter through a pre-rinsed (with DI water) 0.45 um membrane filter.
- Bring sample up to volume of 50 mL and mix.
- Sample is now ready for analysis.

7.6.4 Method 3050B

Used for soils, sludge, sediments, wipes, paint chips, and other miscellaneous solid samples, such as crushed wood or bricks.

- Weigh out a portion of homogenized sample, generally 1.0 – 1.2 grams, into a 100 mL vial. The exact weight is recorded in the TALS digestion spreadsheet. More sample weight may be used if the liquid content is high, as long as the digestion is complete.

NOTE: When using the hot plate/beaker combination, soils are generally weighed to 1.00-2.00 grams. All other volumes are the same as for hot block digestions.

- Add 5 mL of concentrated nitric acid and 5 mL of Milli-Q water.
- Cover the vial with a non-ribbed watch glass and place on a preheated hot block set at 95˚C ± 5°C for 15 minutes without boiling.
- Remove the vial from the hot block and allow to cool 20 minutes.
- Add 5 mL of concentrated nitric acid and reflux for 30 minutes with a non-ribbed watch glass.
- If brown fumes are generated, repeat this last step until no brown fumes are generated indicating complete reaction with the nitric acid.
- Allow the solution to evaporate to a low volume – just enough to cover the bottom of the vial. **Do not allow the sample to boil.** Cover the sample with a ribbed watch glass and heat at 95ºC ±5°C until the volume has been reduced to ~5 mL or for 2 hours without boiling.
- Remove the vial from the hot block and allow to cool for 20 minutes.
- Add 2 mL of Milli-Q water and 3 mL of 30% hydrogen peroxide. If for soil samples, the element Tin is included in the analytes to be reported, the 30% Ultrex II Ultra pure hydrogen peroxide must be used.
- Cover the vial with a non-ribbed watch glass and heat until the reaction is complete.
- Remove the vial from the hot block and allow to cool for 20 minutes.
- Continue to add 30% hydrogen peroxide in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance in unchanged. **Do not add more than a total of 10 mL of hydrogen peroxide.**
- Cover the sample with a ribbed watch glass and heat at 95˚C ± 5˚C until the volume has been reduced to ~5 mL or for 2-hours without boiling.
- Maintain a covering of solution on the bottom of the vial (or beaker) at all times.

If the sample is being analyzed by ICP:

- Allow the sample to cool for 20 minutes
- Add 10 mL of concentrated hydrochloric acid.
- Place the vial on the hot block and heat for 15 minutes without boiling.
- Remove the vial from the hot block and allow to cool for 20 minutes.
- Wash down the sides of the vial with Milli-Q water and filter into a 100 mL snap-cap container through Whatman 541 filter paper.
- Dilute the sample to the 100 mL mark in a snap-cap container.
- The sample is now ready for analysis.

7.7 Documentation

7.7.1 TALS Digestion Spreadsheets

Sample digestion and standard traceability are documented within the TALS ADII spreadsheets. The spreadsheets must be completed for each day's work in real time as the samples are measured and spiked prior to putting them on the hot block. Sample IDs must be scanned into the batches to reduce transcription errors. Any notes relevant to the digestion batch must be made directly in ADII.

The following information must be recorded in the Batch Notes when applicable: Filter Lot #, HCl Lot #, HNO_3 Lot #, H_2O_2 Lot #, Hot Block ID # and Temperature, Thermometer ID #, Start Time, End time, Digestion Tube Lot # and Teflon strips Lot #, Balance ID, pipette ID, Snap Cap Lot#, uncorrected and corrected temperatures.

7.7.2 Traceability of Standards

Custom made and single element stock standard solutions which are traceable to NIST or EPA are purchased. Upon receipt, each standard is entered into the TALs LIMS database and is issued unique source ID #. The manufacturer, lot #, date received, expiration date, and the initials of the analyst are also entered.

8.0 QUALITY CONTROL

8.1 QC Summary

QC Standard	Indicator
Method Blank (MB)	Examined to determine if there was any contamination introduced during the digestion process.
Laboratory Control Sample (LCS)	Used to determine the completeness of the digestion process. The accuracy is measured by the percent recovery (%R) of each standard.
Matrix Duplicate (DU)	Demonstrate analytical precision and is reported as Relative Percent Difference (RPD).
Matrix Spike (MS) / MS Duplicate (MSD)	Used to demonstrate analytical accuracy and is reported as % recovery.
LB (TCLP/SPLP)	Examined to determine if there was any contamination introduced during the extraction process
LCS (TCLP/SPLP)	TCLP/SPLP fluid used for the LCS for TCLP/SPLP samples

8.2 Corrective Action

A Non-Conformance Memo (NCM) will be initiated by the analyst in TALS anytime there is a deviation from the routine preparation procedures, as outlined within this SOP. This includes, but is not limited to: limited sample volume, sample loss due to spills, extremely vigorous reactions, spiking issues or any other issues that may occur during the preparatory procedure. The Section Manager will review the NCM and document any corrective action needed at that time. All analytical 'out-of-control' situations are identified as indicated in the supporting analytical SOP's proper.

9.0 DATA ANALYSIS AND CALCULATIONS

Not Applicable.

10.0 POLLUTION CONTROL

It is Eurofins policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

10.1 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to UP-WM-001.

- Waste from this procedure will enter the "Corrosive Wastewater" wastestream.

11.0 METHOD PERFORMANCE CRITERIA

Refer to sections 1, 6, 7 and 8.

12.0 REFERENCES

Refer to Section 1.0.

13.0 ATTACHMENTS

Appendix A. Metals Digestion Standard Spike Concentrations

14.0 REVISION HISTORY

- Revision 35 was updated on 02/09/24
- External Audit
- Section 7.1 Requirement of matrix matching for soils required for all samples
- Section 7.7.1 Removed reference to Appendix B
- Sections 7.6.1 and 7.6.1.1 filtering is optional

Appendix A.

Metals Digestion Standard Spike Concentration

ICP

Vendor	Stock Name	Elements	Conc. (mg/L)
Environmental Express	HP1381-A-500	Al, Ba	2,000
		Ca, Mg, K, Na	10,000
	HP1381-B-500	Se	10
		Pb	20
		As	40
		Tl, Be, Cd	50
		Cr	200
		Cu	250
		Co, Ni, Li, V, Bi, Mn, Zn	500
		B, Fe, Sr	1,000
	HP1381-C-500	Ag	50
		Sb, P	500
		Mo, Sn, Ti	1,000
		Si	5,000
Inorganic Ventures	Single Element Standard	As	1,000
		Pb	1,000
		Se	1,000
		Tl	1,000

ICP-MS

Vendor	Stock Name	Elements	Conc. (mg/L)
Environmental Express	HP2930-A-500	Al	2,000
		Ca, Mg, K, Na	10,000
	HP2930-B-500	Se	10
		Pb	20
		As	40
		Tl, Be, Cd	50
		Cr	200
		Cu	250
		Ba, Co, Ni, V, Mn, Zn	500
		B, Fe, Sr	1,000
	HP2930-C-500	Ag	50
		Sb	500
		Mo, Sn, Ti	1,000
		Si	5,000
Inorganic Ventures	Single Element Standard	As	1,000
		Pb	1,000
		Se	1,000
		Tl	1,000

TITLE: Wet Chemistry
Inorganic Ions by Ion Chromatography

Approvals (Signature/Date):

Logan Poracky 7/25/24
Logan Poracky Date
Supervisor, Wet Chemistry

Chris Hoham 7/25/24
Chris Hoham Date
Env. Health & Safety Coor.

Nicole Berg 7/25/24
Nicole Berg Date
Quality Assurance Manager

Paul Kolarczyk 7-25-24
Paul Kolarczyk Date
Inorganic Technical Manager

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1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) defines the procedure for determining the following inorganic anions by Ion Chromatography: Fluoride, Chloride, Nitrite-N, Bromide, Nitrate-N, Ortho-Phosphate-P, and Sulfate. This SOP was written using EPA Method 300.0, revision 2.1; and SW 846, Update IV, Method 9056A as references.

On occasion, clients request slight modifications to this SOP for non-drinking water samples. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP), authorized via laboratory signature approval, and mentioned in the data package's case narrative. **Note: Method modifications are not allowed for Drinking Water samples without prior written approval from the US EPA.**

1.1 Method Sensitivity

NOTE: Results of linear range and MDL studies indicate the need for changes in calibration standard concentrations; ICV/LCS concentrations; and reporting limits.

1.1.1 Method Detection Limits

The method detection limit (MDL), referred to as the detection limit (DL) in NELAC documents, is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants" with additional details are provided in the Eurofins Corporate SOP, *NDSC-QA-SOP42091, Detection and Quantitation Limits* and the Eurofins Chicago SOP, *UP-QA-017, Method Detection Limit Studies.* MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; the MDL study will be performed and verified on an annual basis verifying the Lower Limit of Quantitation (LLOQ) for the method.

Attachment 1 (Standards/QC Summary Table) defines the preparation and concentrations of the MDL standards.

1.1.2 Demonstration of Capability

Before the laboratory may institute a new method and begin reporting results, the laboratory shall confirm that it can properly operate the method. A demonstration of capability is performed whenever there is a change in instrument type, method or personnel. An Initial Demonstration of Capability (IDOC) must be thoroughly documented and approved by the Department Manager/Supervisor and QA Manager prior to independently analyzing client samples. All associated documentation must be retained in the QA Department and in the Analyst Training files. For additional details on the demonstration of capability procedures followed, refer to the laboratory SOP, *UP-QA-QAM, Quality Assurance Manual, Sections 19.4.2 and 19.4.3.*

1.1.3 Reporting Limits (RL)

Reporting Limits (equivalent to LLOQ) are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. The laboratory maintains reporting limits that are higher than the MDL. Wherever possible, reporting is limited to values ~3-5x the respective MDL to ensure confidence in the value reported. Client specific requests for reporting to the MDL are special circumstances not to be confused with the previous statement. Refer to Attachment 1 for routine reporting limits, uncorrected for dilution factors, sample weight/volume variances, or moisture content.

1.2 Definitions

Refer to Section 3.0 of the Laboratory's Quality Assurance Manual (UP-QA_QAM).

1.3 Summary of Method

A small volume of sample, typically 10-25 µL (2µL for AS18 KOH method), is introduced into an ion chromatograph (IC). The anions of interest are separated and measured, using a system comprised of a guard column, separator column, suppressor device, and a conductivity detector. For solids, the analysis is preceded by a leaching procedure.

2.0 INTERFERENCES

- Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems.
- Possible interference from the water dip or negative peak that elutes near the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent to 100 mL of each standard and sample.
- Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.
- The quantitation of un-retained peaks should be avoided. Low molecular weight organic acids (formate, acetate, propionate, etc.) which are conductive and co-elute with or near the fluoride peak would bias the fluoride quantitation in some drinking and most waste waters. Ion chromatography is not recommended for analysis of TCLP extracts in which acetic acid is used.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual, Lab Specific Addendum to the CSM, and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coat and closed-toe, nonabsorbent shoes are a minimum.

3.1 Specific Safety Concerns or Requirements

- Potassium Nitrate and Sodium Nitrate are strong oxidizers; therefore, do not store them near any combustible materials. These chemical are stable under prescribed conditions of use and storage (i.e., store protected from air). Note: These chemicals are not routinely use at Eurofins Chicago for IC analysis. They may be used in the event a purchased stock standard becomes unusable and the analyst must prepare a stock locally (refer to source method for instructions). They are kept in inventory.
- Sodium Fluoride is highly toxic. Note: It is not routinely used at Eurofins Chicago, but may be, in the event a fluoride stock must be prepared locally (refer to source method for instructions). It is kept in inventory.
- Exercise caution when using syringes with attached filter assemblies. Application of excessive force has, upon occasion, caused a filter disc to burst during the process.

3.2 Primary Materials Used

Because Eurofins Chicago purchases 1000 mg/L stock standards for IC analysis, the hazardous salts in the table below are not used except in the event that local preparation of a stock becomes necessary.

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material[1]	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Potassium Nitrate	Oxidizer	None	Causes irritation to the respiratory tract, skin and eyes. Symptoms may include coughing, shortness of breath. Symptoms include redness, itching, and pain.
Sodium Fluoride	Poison	2.5 mg/m^3-TWA as F	**Highly Toxic.** Causes severe irritation to the respiratory tract, symptoms may include coughing, sore throat, and labored breathing. Causes irritation, with redness and pain. Solutions are corrosive. Eye irritant! May cause irritation and serious eye damage. Effects may not appear immediately.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.

[1] – Always add acid to water to prevent violent reactions.
[2] – Exposure limit refers to the OSHA regulatory exposure limit.

4.0 EQUIPMENT AND SUPPLIES

- Dionex ICS-1100 Ion Chromatograph (IC6;IC8) with Chromeleon v. 7.2 software
- Thermo Scientific Integrion RFIC
- Ionpac AG22, (4 X 50 mm) Guard Column, PN 064139
- Ionpac AS22 (4 X 250 mm) Analytical Column, PN 064141
- Ionpac AS18 Fast Analytical Column, PN 075760
- Ionpac AG18 Guard Column, PN 075762
- Dionex EGC 500 KOH Cartridge, PN 075778
- Dionex CR-ATC 600 Anion Trap Column, PN 088662

- DRS 600 4 mm Suppressor, or equivalent
- Dionex Automated Samplers, AS-AP
- 1.5 mL vials with filter caps for Automated Sampler
- Class A volumetric flasks, various sizes
- Eluent reservoirs
- AS-AP Vial Tray (40 position)
- 5 or 10 mL syringes
- 0.45 um syringe filters
- Class A graduated cylinders
- Balance capable of weighing to the nearest 0.1g
- Chrom - chromatography software for data analysis
- Quantabs chloride strip 300-6000 ppm Cl^- or equivalent
- Quantabs sulfate strip 200-1600 ppm SO_4 or equivalent

5.0 REAGENTS AND STANDARDS

5.1 Stock Standards

5.1.1. Stock standards are purchased from an approved vendor. If no expiration date is provided, the stock standard solutions may be used for up to one year from open date and must be replaced sooner if verification from an independent source indicates a problem.

5.2 Intermediate / Working Standards

5.2.1. Intermediate / Working standards are prepared as dilutions from the stock standards. Intermediate / working standard solutions shelf life and are stored according to table below.. The intermediate / working standard solution must be replaced if verification from an independent source indicates a problem. Refer to the LIMS standards and reagents module for further details on preparation of intermediate / working standard solutions.

Reagent	Shelf Life	Storage Requirements
Eluent (100x Conc)	6 months	None
Eluent Working (1:10)	6 months – Not to exceed Eluent expiration date	None
Various Anions Stocks	Manufacture's recommendation	Manufacture's recommendation

5.3 Quality Control Preparation

Refer to Attachment 1 for concentrations and preparation from Stock I for AS22 carbonate method. Refer to Attachment 2 for AS18 KOH method.

Note: MS/MSDs will most likely need to be done on multiple sample dilutions. Calculate and report matrix spikes on the same dilution from which the original sample is reported. As long as the original sample concentrations fall within the range of the calibration curve for each analyte, the MS/MSD will be reported and "E" flagged if it exceeds the calibration range.

6.0 CALIBRATION (NON-DAILY)

The calibration curve is prepared whenever a significant change in instrument response is observed. Calibration curves need to be prepared with freshly made standards to ensure ongoing

accuracy of data. Some examples of the need for recalibration may include low recovery or concentration of the ICV standard, significant changes in retention times of the anions, or instrument maintenance, which may affect the chromatography. Some sample matrices will affect the retention times of subsequent injections. The calibration is checked immediately after the curve with an ICV with the requirement of ±10% acceptance criteria. (Refer to Section 7.4) Refer to the Eurofins Corporate Policy for Calibration Curves and the Selection of Calibration Points (NDSC-US TSO-QP44940) *and the Selection of Calibration Points* and the *Calibration Criteria Training, Inorganics* Document CHI-22-09-472 for further guidance.

Note: A low level and a high level verification check standard (ICVL and ICVH) are required to be analyzed after the CCV/CCB when samples that need to follow the BP LaMP protocol are analyzed, if the calibration curve is not analyzed on the same day as the samples. Control limits of 90-110% will be applied. The ICVL is equivalent to the current CCV standard. The ICVH will be prepared at the anion levels of Standard 5 of the calibration curve.

No blank is analyzed as part of the curve, the curve for each anion consists of 6 mixed standards, each of which contains a given concentration of each of the seven anions. The lowest point in the curve is at the lower limit of quantitation (LOQ; RL) and the high point in the curve is the linear range of the instrument.

6.1 Retention Times (RTs)

RTs may vary according to ionic size, ionic charge, ion concentration, column type, and ionic composition of the mobile phase. The RT window will be routinely determined using +/- 2% of the RT for each analyte contained in the Continuing Calibration Verification (CCV) standard.

Method 9056A suggests the retention time be established based on 3X the standard deviation for each analyte over a 24-hour period. Eurofins Chicago does not have sufficient points in a 24-hour period, but determines the standard deviation of standards over a period of several days annually and calculates the retention time window. If the +/-2% window is comparable, Eurofins Chicago will continue to use that method, but will keep the other data on file.

Analyst discretion may be used for RT shifts resulting from complex sample matrices. The instrument must be recalibrated or obtain section manager or QA approval if the RT drifts outside this window. RTs may vary with the use of different columns.

Beware that the retention order on the AS22 Carbonate and AS18 KOH methods are different, see Attachment 2.

7.0 PROCEDURE

7.1 Quality Control Checks, non-calibration

Quality Controls	Frequency [1]	Default Control Limits
Method Blank (MB)	1 / set of < 20 samples	< Reporting Limit <1/2 RL (per QAPP) < MDL (Drinking Water)
LCS[2,3]	1 / set of < 20 samples	80-120% recovery (9056A) 90-110% recovery (300.0) ≤15 RPD (9056A) ≤20 RPD (300.0)
MS / MSD [4]	1 / 10 samples ((300.0) 1 / 20 samples (9056A)	80 – 120% recovery ≤15 RPD (9056A) ≤ 20 RPD (300.0)

Quality Controls	Frequency [1]	Default Control Limits
Duplicate (DU)[4,5]	1 / 10 samples (DW)	≤ 15 RPD (9056A) ≤ 20 RPD (300.0) ± 5X the RL

[1] Client-specific QAPPs may include QC limits and frequency requirements that supersede those given above. Certain client QAPPs may require additional QC types, such as an MRL to be run in sequence.
[2] Statistical control limits are available for those clients or projects that require the use of statistical limits.
[3] LCS Duplicate (LCSD) is performed only when insufficient sample is available for the MS/MSD or when requested by the client/project/contract.
[4] Unless specified, the sample selection for matrix QC is rotated among client samples so that various matrix problems may be noted and/or addressed. Client samples identified as a blank shall not be used for MS/MSD analysis.
[5] For analysis of non-drinking water samples by 9056A and 300.0, MS and MSDs are the default matrix QC, and a DU is only done by client or program request.

Note: Drinking water samples are analyzed in sets of 10 with an MS and DU performed on the drinking water matrix. Control limits are ≤ 10 RPD for duplicates and 85 - 115% for matrix spikes. LCS recoveries must be 90 - 110%.

Note: The MB and LCS must be treated exactly like the samples in order to make a valid assessment of the contamination level. This includes filtration (documented in the TALs filtration batch) and any other sample handling techniques. Per special QAPP requirements (BP LaMP for example) when solids are prepped, a solid matrix (such as Teflon or Hengar boiling chips) must be used in the leaching of the MB and LCS.

7.2 Sample Preservation and Storage

Samples should be collected in scrupulously clean glass or polyethylene bottles.

Anion	Preservation	Hold Time
Fluoride Chloride Bromide Sulfate	Cool to ≤ 6°C	28 Days
Nitrite-N Nitrate-N Ortho-Phosphate-P	Cool to ≤ 6°C	48 Hours

7.3 Sample Preparation

7.3.1 Waters

All water samples and the associated MB and LCS are filtered prior to analysis using a 0.45 µm membrane type filter, the filter ID is documented in the batch information screen in TALs. If transition metals are known or suspected to be present in a sample, it is good practice to make a high dilution to protect the guard columns prior to analysis, since transition metals will corrupt the columns. Use these columns with care and appropriate rinsing.

7.3.2 Soils

Weigh ~10 grams weighed to the nearest 0.1 gram of the homogenized solid sample into a 100 mL digestion vessel (Confirm that metals prep has verified vessel lot) (per section 11.7 of method 300.0). The LCS and MS/MSD are spiked, prior to addition of the 100 mL of reagent grade water. Note: The MS/MSD spike is added directly onto the sample to increase the contact time between the spike and the sample. Mix the solution well using a wrist action shaker for 10 minutes, and then filter the slurry solution using a 0.45 µm membrane type filter. (Allowing the slurry solution settle for few hours prior to filtering will allow the particulates to settle, yielding an easier filtration process. **Never compromise the representative composition of the sample in the original container!** Centrifuging is another pre-filtration option.) If transition metals are known or suspected to be present in a sample, it is good practice to make a high dilution to protect the guard columns prior to analysis, since transition metals will corrupt the columns. Use these columns with care and appropriate rinsing.

7.4 Calibration /Calibration Verification[1]

Calibration Controls	Sequence / Frequency	Control Limit
Standard Curve[2] (Linear-1st Order)	As needed	r ≥ 0.995; Stds. 3 at ± 10% of known; x-intercept < Reporting Limit (RL)
ICV (Initial Calibration Verification)	Immediately after curve	± 10%
ICB (Initial Calibration Blank)	After ICV	< RL <1/2 RL (per QAPP)
ICVL (low-level ICV)[3]	After CCB	± 10%
ICVH (high level ICV)[3]	After ICVL	± 10%
CCV (Cont. Calibration Verification)	After every 10 readings and after last sample reading	± 10%
CCB (Cont. Calibration Blank)	After every CCV	< RL <1/2 RL (per QAPP)

[1] See Attachment 1 for details of standard preparation.
[2] The lowest standard in each curve is at the Eurofins Chicago lower limit of quantitation (RL, referred to as LOQ in NELAC) and must be within 50% of the true value for 9056A. The remaining standards should be within 10% of the true value.
[3] *The ICVL and ICVH are required to be analyzed to meet the BP LaMP Protocol if the calibration curve is not analyzed on the same day as the samples.*
[4]Quadratic regression cannot be used for bromide and sulfate for samples from the state of South Carolina. If quadratic regression is used the state of Wisconsin require an additional CCVH at 40ppm alongside the CCV at 10ppm

7.5 Preventive Maintenance

Instrument maintenance is recorded in the instrument maintenance log. The following checks are completed as necessary to ensure efficient operation of the instrument.

- Check for leaks or spills within the valve compartments. Isolate and repair any leaks.
- Clean up any spills immediately.
- Rinse any dried eluents or reagents off the system components with DI water.

- Check all liquid lines for discoloration or crimping. Relocate pinched lines and replace damaged lines.
- Change eluent reservoir filter and in-line filters as needed.
- Some sample matrices will degrade the IC components over time. Placing one to three vials containing concentrated eluent in the schedule after the final CCB may help to prevent the degradation.
- Replace guard column pre-filter routinely, approximately every 2-4 weeks.
- Clean the columns periodically as needed following the Dionex manuals. Be sure to place the guard column after the separator column for this procedure.

7.6 Sample Analysis

Create a worklist in Chrom (TALS). Be sure to include sample dilutions and sample reagents for accurate calculation of results.

Set up a schedule in Chromeleon, performing the following steps:

- Under Chromeleon console > Data Tab. This should pull up the last schedule created.
- To copy for a new run, click on: File > “Save As…” > type in the worklist number
- Click “Save”.
- Scan in the worklist IDs with their associated tray positions.

Any calibration blank or standard that is repeated during the run can be poured into a single reagent vial and placed in the reagent vial portion of the autosampler carousel. Be sure to enter the correct vial location in the schedule.

Add 10 µL of eluent per 1 mL of sample to each vial (samples, standards and QC) to help eliminate the negative baseline (water dip).

7.6.1 General Operating Conditions

Fill the eluent reservoir with working eluent solution (reagent 5.2). Eluent will need to flow through the system until it is equilibrated or for an hour before starting. Start the run when the instrument’s general operating conditions are met (see following table). Refer to the instrument’s operational manual for complete details.

IC 6 & IC 8	
Item	**AS22 Carbonate Method**
Sample Loop Volume	10 µLs
Analytical Column	Ionpac AS22 (4 X 250 mm)
Eluent	4.5 mM Na_2CO_3 / 1.4 mM $NaHCO_3$
Eluent Flow Rate	1.2 mL / min
Suppressor	DRS 600, 4mm @ 31mA
Background Conductivity	~ 25 µS (stable)
System Pressure	1500 – 2500 psi (stable)

7.7 Documentation

7.7.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

7.7.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

7.7.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs are scanned and attached to the Documents section in the LIMS analytical batch.

7.7.4. Record all sample results and associated QC directly into LIMS. Level I and Level II reviews are performed in LIMS.

Examples of items included in the above reviews are as follows:

- QC data are outside the specified control limits for accuracy and precision
- Unusual detection limit changes are observed
- Samples having unusually high results
- Samples exceeding a known regulatory limit
- Raw data indicating some type of contamination or poor technique
- Inconsistent peak integration (if applicable)
- Transcription errors
- Results outside of calibration range

8.0 QUALITY CONTROL

8.1 QC Summary

8.1.1 One MB and one LCS will be included in each batch of samples (refer to Section 7.1). The MB will be examined to determine if contamination is being introduced in the laboratory. The LCS will be examined to determine accuracy of the method and cumulative LCS data will provide precision data.

8.1.2 Accuracy will be measured by the percent recovery (%) of the LCS. The recovery must be in range, as determined by in-house control limits or statistical analysis, in order to be considered acceptable. Precision will be measured by the cumulative reproducibility of the LCSs.

8.1.3 One MS/MSD (or MS/DU) is required per matrix per sample batch (refer to Section 7.1), unless otherwise requested. Results must agree within the limits defined in Section 7.1 or within internally-derived statistical limits in order to be considered acceptable.

8.2 Corrective Actions

When an out-of-control situation occurs, the analysts must use their best analytical judgment and available resources to determine the corrective action to be taken. The out-of-control situation may be caused by more than one variable. The analysts should seek the assistance of their immediate supervisor or manager, QA personnel, or other experienced staff if they are uncertain of the cause of the out-of-control situation. The analysis must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out of control situation should be reanalyzed. Out-of-control data must never be released without approval of

the Supervisor, Technical Director, Operations Manager, Project Manager, QA Manager or the Lab Director.

Listed below are steps that MUST be taken when an out of control situation occurs:

- demonstrate that all the problems creating the out of control situation were addressed;
- document the problem and the action which was taken to correct the problem on the data review checklist;
- document on the checklist that an in-control has been achieved; and write the appropriate Non-Conformance Memo (NCM) in the batch;
- receive approval (signature) of the Supervisor, Operations Manager, Technical Director, QA Manager, Project Manager, or the Laboratory Director prior to the release of any analytical data associated with the problem.

It may be necessary to forward an NCM to the PM/Client for further action/approval prior to reporting of the data.

The following are suggested actions to specific out of control situations:

QC Standard	Suggested Corrective Actions
Calibration Curve	• reanalyze the standard curve; • prepare a new stock and/or working standards; • check the reagents/solutions and prepare fresh if necessary.
ICV (ICVL, ICVH)	• repeat the ICV to verify proper preparation; • prepare a new ICV from the original stock; • check for instrument base-line drift; • restandardize the instrument with existing standards, reanalyze; • check the reagents/solutions and prepare fresh if necessary; • prepare a new stock and/or working standards and recalibrate.
ICB	• prepare a new ICB to verify proper preparation; • verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability; • determine the source of contamination by the process of elimination, correct the problem and reanalyze. (Carry over from a previous analysis and reagent contamination are two common sources).
MRL	• repeat the MRL to verify proper preparation; • prepare a new MRL from the original stock; • check for instrument base-line drift; • restandardize the instrument with existing standards, reanalyze; • check the reagents/solutions and prepare fresh if necessary; • prepare a new stock and/or working standards and recalibrate.
LCS	• reanalyze the LCS to verify that an out-of-control situation exists; • determine the source of the error within the preparation procedure, correct the problem and repeat the sample set. (Sources of contamination could be either from the reagents, the LCS stock solution, or the preparation area.) • Note any out-of-control LCSs on the data review checklist and in an NCM.
LCSD	• If an LCS Duplicate (LCSD) is required, it must meet the control limits of ≤ 20 RPD. If this criteria is not met, and both LCS's meet the % Recovery control limits, then see your supervisor for proper corrective action.

QC Standard	Suggested Corrective Actions
MB	• Reanalyze the MB to verify contamination at a level > Reporting Limit; • Determine the source of contamination and correct the problem; • All samples whose concentration is <10 times the contaminated MB level must be reprocessed and reanalyzed; any sample which is >10 times the MB level need not be reanalyzed. However, note the out-of-control MB on the data review checklist and write an NCM. • If the sample is a non-detect for the parameter in question, the MB is appropriately flagged in TALS and the samples are reported without further corrective action, according to the client/project/QAPP requirements and may contain an NCM noting the presence of contamination in the blank. • If the sample concentration is above the RL, the MB and sample are appropriately flagged in TALS. Further corrective action (re-analysis of samples) is dependent upon client/project/QAPP requirements. At least, the samples will be flagged and an NCM will note the presence of the analyte in the MB. The report format will be consistent with client/project/QAPP requirements. • If the sample concentration is between the MDL and the RL, the sample data are reported as estimated and flagged for the presence of the analyte in the MB. The report format and additional corrective action is dependent upon client/project/QAPP requirements. • In all cases, MB data is used to assess contamination in the laboratory environment. Samples associated with MBs above the MDL will be evaluated, and at a minimum will be flagged in both TALS and in the final deliverable, and an NCM/narrative will note the problem. Additional corrective action is client/project/QAPP dependent. • MB data will be monitored to ensure that a systematic cause or source of contamination is not being introduced into the system. Upon evidence to that effect, the lab will take immediate corrective action to identify the source and correct the problem. Any associated samples analyzed during that time will be evaluated and suspect samples will be reanalyzed if appropriate.
DU	• the sample must be reprocessed and reanalyzed unless the sample concentration is <5 times the Reporting Limit, then the ± Reporting Limit rule applies; • if the reanalysis is within the control limits, the second value is reported; • if the reanalysis is still outside of the control limits, the data must be flagged and noted in an NCM.
MS	• If a single spike is performed and it is outside the acceptance limits, it must be repeated to verify the matrix effect. Generally, an MS and MSD are performed together in the same batch as the original sample analysis. • Report all spikes, whether or not they are in control. • Note out-of-control spikes on the data review checklist and NCMs.
CCV	• repeat the CCV to verify proper preparation; • report non-detect sample results if the CCV bias is high; write an NCM • reanalyze all samples associated with a low biased CCV; • prepare a new CCV from the original stock; • check for instrument base-line drift; • check the reagents/solutions and prepare fresh if necessary; • recalibrate with a new standard curve and repeat all detected (if CCV is biased high)samples since the previous in-control CCV; • never dispose of any samples until you are sure that all QC are within their designated control limits.

QC Standard	Suggested Corrective Actions
CCB	• prepare a new CCB to verify proper preparation; • verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability; • determine the source of contamination by the process of elimination, correct the problem and reanalyze all the samples since the previous in-control CCB. (Carry over from a previous analysis or reagent contamination are two common sources); • never dispose of any samples until you are sure that all QC are within their designated control limits. • Report only non-detects and samples >10X the contamination level. Write an NCM

9.0 Data Analysis and Calculations

9.1 Sample Concentrations

9.1.1 Waters

$$\frac{\text{mg}}{\text{L}} = \text{instrument reading} \times \text{dilution factor}$$

9.1.2 Soils

$$\frac{\text{mg}}{\text{Kg}} = \frac{\text{instrument reading } \left(\frac{\text{mg}}{\text{L}}\right) \times \text{final vol.(mL)}}{\text{sample wt.(g)}} \times \text{dilution factor}$$

9.2 Accuracy

9.2.1 ICV/CCV and LCS % Recoveries

$$\frac{\text{Observed concentration}}{\text{Actual concntration}} \times 100$$

9.2.2 MS % Recovery

$$\frac{(\text{Spike sample conc.} - \text{Original sample conc})}{\text{Spike concntration}} \times 100$$

9.3 Precision

9.3.1 Matrix Dup. and LCD Relative Percent Difference (RPD)

$$\text{RPD} = \frac{|\text{Org.sample value} - \text{dup.sample value}|}{\left[\frac{\text{orig.sample value} + \text{dup.sampe value}}{2}\right]} \times 100$$

9.4 Manual Integration Policy

In each case where the file has been edited or manual integrations have been performed, the following guidelines apply:

- Manual integrations should be consistent among all files integrated.
- Manual integrations should not be performed solely to meet QC criteria.
- Excessive manual integrations may reflect an instrumental or methodological problem that should be addressed.
- Manual integrations shall follow the Eurofins Corporate SOP for manual integrations (NDSC-ETHC-SOP43862).

Manual integrations are most often performed for the following reasons:

- Assignment of correct peak that was mis-identified by the data system.
- Incomplete auto-integration due to high level of target compound detected.
- Incomplete auto-integration due to background interference.
- Incorrect auto-integration due to co-elution or near co-elution of compounds.
- Missed peaks.

All integrations are reviewed by the analyst. Manual integrations in Chrom require a reason code to be selected prior to making any changes to the data. Chrom automatically records the chromatogram before and after the manual integration. All manual integrations must be reviewed during the second level data review process.

10.0 POLLUTION CONTROL

It is Eurofins policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

10.1 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to UP-WM-001.

The following waste streams are produced when this method is carried out.

- Waste from this procedure will enter the “Wastewater” wastestream.
- Single component standards will be turned over to the EHSC or Waste Technician.

11.0 METHOD PERFORMANCE CRITERIA

Refer to Sections 1, 6, 7 and 8.

12.0 REFERENCES

Refer to Section 1.0

13.0 ATTACHMENTS

Attachment 1: Example: IC Standards / QC Summary Table
Attachment 2: Example: IC9 Standards / QC Summary Table
Attachment 3: Export .CSV data

14.0 REVISION HISTORY

- Revision 26 updated on 04/30/24
- Internal Audit
- Throughout added information for KOH method for IC9
- Section 4.0 updated with IC9 instrument and supplies
- Section 5.0 was rewrote
- Section 6.0 removed requirement of monthly calibration
- Section 7.1 removed reference to 9056
- Section 7.6 Updated Chromeleon sequence is saved as worklist number
- Section 7.7 was rewrote
- Section 9.4 corrected corporate SOP reference.

Attachment 1

Calibration & QC Standards for IC Methods 300 & 9056A

Eluent Stock (450mM Na_2CO_3 : 140 mM $NaHCO_3$) – Expiration 6 months

Sodium Carbonate (g)	Sodium Bicarbonate (g)	Diluent	Final Volume (mL)
47.7	11.76g	Milli Q H_2O	1000

Working Eluent (4.5mM Na_2CO_3 : 1.4 mM $NaHCO_3$) for standard dilution – Expiration 6 months

Purpose	Eluent Stock (mL)	Diluent	Final Volume (mL)
STD dilution	1	Milli Q H_2O	100
For IC	20	Milli Q H_2O	2000

IC High Standard (Std 6, 50 ppm) – Expiration 1 month

F^- (mL)	Cl^- (mL)	NO_2^- (mL)	Br^- (mL)	NO_3^- (mL)	PO_4^- (mL)	SO_4^{2-} (mL)	Eluent Stock (mL)	Diluent	Final Volume (mL)
5	5	5	5	5	5	5	1	Milli Q H_2O	100

Calibration Standards – Expiration 1 month

Standard*	IC High STD (mL)	Diluent	Final Volume (mL)
1	0.2	Milli Q H_2O	10
2	1	Milli Q H_2O	10
3	2	Milli Q H_2O	10
4	4	Milli Q H_2O	10
5	8	Milli Q H_2O	10
6	10	NA	10

*Entered into worklist as listed above

QC Standards

STD	IC High STD (mL)	Eluent Stock (mL)	Diluent	Final Volume (mL)
CCV (10ppm)	2	1	Milli Q H_2O	10
CCVH (40 ppm)	8	1	Milli Q H_2O	10
MDLS (1ppm)	0.2	1	Milli Q H_2O	10
MDLV (0.5ppm)	0.1	1	Milli Q H_2O	10

QC Standards Stock II

STD	F^- (mL)	Cl^- (mL)	NO_2^- (mL)	Br^- (mL)	NO_3^- (mL)	PO_4^- (mL)	SO_4^{2-} (mL)	Eluent Stock (mL)	Diluent	Final Volume (mL)
ICV/LCS (20ppm)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.25	Milli Q H_2O	25
MS/MSD	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	Sample	10

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Attachment 2

Calibration & QC Standards for IC Methods 300 & 9056A
IC 9 Only

STD 8 - Expiration 1 month

F^- (mL)	Cl^- (mL)	NO_2^- (mL)	Br^- (mL)	NO_3^- (mL)	PO_4^- (mL)	SO_4^{2-} (mL)	Diluent	Final Volume (mL)
5	25	5	5	5	5	25	Milli Q H_2O	100

Calibration Standards – Expiration 1 month

Standard*	STD 8 (mL)	Diluent	Final Volume (mL)	QC
1	0.04	Milli Q H_2O	10	
2	0.2	Milli Q H_2O	10	
3	1	Milli Q H_2O	10	
4	2	Milli Q H_2O	10	CCVL
5	4	Milli Q H_2O	10	CCV
6	6	Milli Q H_2O	10	CCVH
7	8	Milli Q H_2O	10	
8	10	NA	10	

*Enter into worklist as listed above

Calibration Final Concentrations (ppm)

STD LV	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^-	SO_4^{2-}
1	0.2	1	0.2	0.2	0.2	0.2	1
2	1	5	1	1	1	1	5
3	5	25	5	5	5	5	25
4	10	50	10	10	10	10	50
5	20	100	20	20	20	20	100
6	30	150	30	30	30	30	150
7	40	200	40	40	40	40	200
8	50	250	50	50	50	50	250

QC Standards Stock II

STD	F^- (mL)	Cl^- (mL)	NO_2^- (mL)	Br^- (mL)	NO_3^- (mL)	PO_4^- (mL)	SO_4^{2-} (mL)	Diluent	Final Volume (mL)
ICV/LCS[1]	0.5	2.5	0.5	0.5	0.5	0.5	2.5	Milli Q H_2O	25
MS/MSD	0.1	0.5	0.1	0.1	0.1	0.1	0.5	Sample	10

[1] Volumes can be adjested proportionately to make larger/smaller amounts of standard

Approximate RT and Eluation Order

F^-	Cl^-	NO_2^-	SO_4^{2-} *	Br^- *	NO_3^-	PO_4^-
2.043	2.797	3.33	3.873	4.52	5.297	7.363

*Changing the eleunt concnetration will impact the elution order of sulfate/bromide

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Attachment 3.

Export Data

Eurofins Chicago

Ion Chromatography .CSV Export

To export:

1. From Chromeleon Console, go to Data Tab > Have the data from the run you want to export on screen. Hit F5
2. Highlight samples to export.
3. Right click and select "Export".
4. Click "OK" to generate export report.

CHI-22-12-191/A-04/24

TITLE: WET CHEMISTRY
Alkalinity

Approvals (Signature/Date):

Logan Poracky 8/2/24
Logan Poracky Date
Supervisor, Wet Chemistry

Chris Hoham 8/2/24
Chris Hoham Date
Env. Health & Safety Coor.

Nicole Berg 8/2/24
Nicole Berg Date
Quality Assurance Manager

Paul Kolarczyk 8-2-24
Paul Kolarczyk Date
Inorganic Technical Director

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1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) is used to determine the alkalinity in drinking, surface, and ground waters, and solid matrices. This SOP was written using Standard Methods 2320B-1997; 2320B-2011 and 2320B-2021 as the primary reference and 2020 A and B for additional QC notes.

Alkalinity is useful in the evaluation and treatment of natural and waste waters, such as it's suitability for irrigation; it's estimated concentrations of carbonates, bicarbonates, and hydroxides; and the functional health and control of water treatment facilities.

Method SM2320B is also used to calculate Free and Total CO2 as defined in SM4500-CO2_D.

On occasion, clients request slight modifications to this SOP for non-drinking water samples. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP), authorized via laboratory signature approval, and mentioned in the data package's case narrative. **Note: There are no method modifications allowed for Drinking Water samples without prior written approval from the US EPA.**

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants" with additional details are provided in the Eurofins Corporate SOP, *NDSC-US-TS-SOP42091, Detection and Quantitation Limits* and the Eurofins TestAmerica Chicago SOP, *UP-QA-017, Method Detection Limit Studies.* MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; the MDL will be performed and verified on an annual basis verifying the Lower Limit of Quantitation (LLOQ) for the method.

1.1.2 Demonstration of Capability

Before the laboratory may institute a new method and begin reporting results, the laboratory shall confirm that it can properly operate the method. A demonstration of capability is performed whenever there is a change in instrument type, method or personnel. An Initial Demonstration of Capability (IDOC) must be thoroughly documented and approved by the Department Manager/Supervisor and QA Manager prior to independently analyzing client samples. All associated documentation must be retained in the QA Department and in the Analyst Training files. For additional details on the demonstration of capability procedures followed, refer to the laboratory SOP, *UP-QA-QAM, Quality Assurance Manual, Sections 19.4.2 and 19.4.3.*

1.1.3 Reporting Limits (LLOQ)

Reporting Limits (LLOQ) are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and

client requirements. The laboratory maintains the reporting limits to values ~3-5x the respective MDL to ensure confidence in the value reported.

Matrix	Reporting Limit
Waters	5 mg/L as $CaCO_3$
Wastes/Soils	0.05% (500 mg/kg) as $CaCO_3$

1.1.4 Definitions

Refer to Section 3.0 of the Laboratory's Quality Assurance Manual (UP-QA_QAM).

1.2 Summary of Method

Alkalinity is the quantitative capacity of an aqueous medium to react with hydrogen ions. Hydroxide (OH^-), carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) anions expressed as calcium carbonate are responsible for the measure of alkalinity.

Hydroxyl ions present in solutions, as a result of dissociation or hydrolysis of solutes, react with additions of standard acid. In titration of a single ionic species, as in the standardization of reagents, the most accurate endpoint is obtained at the inflection point of the titration curve. The inflection point is the point at which a pH change per milliliter of added acid versus volume of acid added is the maximum. Because accurate identification of inflection points may be difficult or impossible in buffered or complex mixtures, the titration is carried to arbitrary endpoints.

Although color indicators may be used (phenolphthalein for 8.3 and bromcresol green or a mixture of bromcresol green - methyl red for 4.5), the endpoint is monitored potentiometrically at Eurofins Chicago using a ManTech PC Titrate auto-titrator. Total alkalinity, with the endpoint pH 4.5, is reported most commonly, but regardless of the species requested, the PC Titrate is programmed to record and calculate total, phenolphthalein, carbonate, bicarbonate, and hydroxide alkalinity for all samples.

All samples are initially titrated with 0.02 N titrant, and samples that are over-range are then re-analyzed in a separate run with 0.1 N titrant.

2.0 INTERFERENCES

- Soaps, oily matter or suspended solids may coat the glass electrode and cause a sluggish response.
- The interfering materials may not be removed to increase precision because some may contribute an important part of the acid-consuming property.
- Similarly, the development of a precipitate during titration may make the glass electrode sluggish and cause high results.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual, Lab Specific Addendum to the CSM, and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under

the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coat and closed-toe, nonabsorbent shoes are a minimum.

3.1 Specific Safety Concerns or Requirements

Although titrant solutions are relatively weak, caution must be exercised during the preparation and handling of these solutions.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE:** This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material[1]	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydrator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
[1] – Always add acid to water to prevent violent reactions. [2] – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 EQUIPMENT AND SUPPLIES

- ManTech Pro PC1000-1136
- ManTech PC Titrate configured for alkalinity with pH probe and ATC and including the following component model numbers: PC-1104-00, PC-1300-475, PC-1000-550, PC-1000-102/4
- TitraPRO2 pH combination Electrode with KCl filling solution and a detachable electrode cable, ManTech part numbers PCE-80-PH1200 (probe) and PCE-86-EX1001 (cable)*
- Compatible auto sampler
- 50 mL centrifuge tubes compatible with autosampler
- Class A glassware
- Eppendorf pipets

* The use of gel-filled or epoxy bodied electrodes has been shown to be less successful with this instrument, resulting in a low bias.

5.0 REAGENTS AND STANDARDS

5.1 Stock Standards

5.1.1. Stock standards are purchased from an approved vendor. If no expiration date is provided, the stock standard solutions may be used for up to one year from open date and must be replaced sooner if verification from an independent source indicates a problem.

5.2 Intermediate / Working Standards

5.2.1. Intermediate / Working standards are prepared as dilutions from the stock standards. Intermediate / working standard solutions shelf life and are stored according to table below.. The intermediate / working standard solution must be replaced if verification from an independent source indicates a problem. Refer to the LIMS standards and reagents module for further details on preparation of intermediate / working standard solutions.

Reagent	Shelf Life	Storage Requirement
pH 4 Buffer	1 year or manufacturer recommendation	None
pH 7 Buffer (need 2 different sources)	1 year or manufacturer recommendation	None
pH 10 Buffer	1 year or manufacturer recommendation	None
Sodium Carbonate (Na_2CO_3) Solution, 0.05 N [1]	1 week	None
~0.1 N Sulfuric Acid (H_2SO_4)	Manufacturer recommendation	None
~0.02 N H_2SO_4	Manufacturer recommendation	None
Potassium Hydrogen Phthalate (KHP) Solution, ~0.05 N [1]	1 year	None
0.1 N Sodium Hydroxide (NaOH) [1, 2]	1 year	None

[1] Only required if 0.1 N and 0.02 N sulfuric acid tritants are prepared and standardized in-house.
[2] Since NaOH is used a standard, it must be standardized when prepared

5.2.2 Standardization

Transfer 20.0 mLs of KPH into a small beaker on a stir plate, using a 20.0 volumetric pipet. Add sufficient DI water to allow gentle stirring with a small stir bar. Add a few drops of phenolphthalein indicator. The solution will be colorless.

Rinse and then fill a 25.0 mL buret with the 0.1 N NaOH. Titrate, slowing as you near the pink endpoint. Record the mL of NaOH required to reach the endpoint, and determine the normality using the following equation:

N x vol = N x vol

Or specifically:

N of NaOH x mL of NaOH = 0.05 x 20.0mL

Adjust the N to 0.10 ± 0.005 if necessary by adding water or NaOH.

The alkalinity in this standard is hydroxide alkalinity, and is reported as total alkalinity only. The other species will be calculated as non-detects or nearly non-detects and must be rejected in the analytical batches.

5.7 Standards Preparation

QC Solution	Preparation
Initial Calibration	4.0, 7.0, and 10.0 pH Buffers
Initial and Cont. Calibration Verification (PHC), after calibration and every 10 readings	Alternate source 7.00 pH Buffer
Lab Control Sample (LCS)[1] (100 mg/L, total alkalinity only), one per 20 or fewer samples	1 mL Stock Sol. 0.1 NaOH to 50 mLs DI Water
Method Reporting Limit (MRL) (5 mg/L, per QAPP or annual MDL study)	50 uL Stock Sol. NaOH to 50 mLs DI Water
MDL Check (MDLV) (2.5 mg/L, with annual MDL study)	25 uL Stock Sol. NaOH to 50 mLs DI Water

[1] An LCS duplicate (LCSD) is sometimes required by client-specific QAPPs.

6.0 CALIBRATION (NON-DAILY)

Not applicable.

7.0 PROCEDURE

7.1 Quality Control Checks

Calibration/QC Standards	Frequency	Control Limit
Method Blank (MB)	1 in 20 samples	< Reporting Limit < MDL (Drinking Waters)
Laboratory Control Standard (LCS)	1 in 20 samples	90 – 110% Recovery
Matrix Duplicate (DU) [1]	1 in 20 samples	≤ 20 RPD

[1] The sample selection for the DU, if not defined by the client on the chain-of-custody, is rotated among client samples so that various matrix problems may be noted and/or addressed.

7.2 Sample Preservation and Storage

Holding time, preservation techniques and sample container may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client request. Listed below are the holding times and the references which include container and preservation requirements for compliance with the Clean Water Act (CWA) and Safe Drinking Water Act (SDWA).

Regulation	Holding Time	Preservation	Reference
CWA	14 days	Cool 0-6ºC	40 CFR Part 136.3
SDWA	14 days	Cool 0-6ºC	EPA 600/4-79-020

7.3 Sample Preparation

7.3.1 Sample Size

This method is for all concentration ranges of alkalinity.

Do not filter, dilute, or otherwise alter aqueous samples. Consult the Supervisor or Project Manager if a sample is biphasic or contains significant solids so as the operation of the instrument might be adversely affected.

Matrix	Sample Size
Waters	~50 mLs (Fills the autosampler tube. 25 mL is titrated by PC Titrate)
Wastes	≥1.0 g/100 mLs DI Water[1]. Use ~50 mL of the extract in autosampler.

[1] Extract for 10 minutes on a wrist-action shaker, allow settling, then gravity filter using glass fiber filters.

7.4 Calibration / Standardization

Calibration/QC Standards	Frequency	Control Limit
4, 7, and 10 buffers	Initial Calibration	See pH electrode manual
pH 7.0 (as ICV,CCV)	Initially, every 10 readings, and at the end of the run	± 0.1 pH unit

7.5 Preventive Maintenance

Occasionally, and anytime there is a consistent bias in the MB or LCS, the pH probe should be thoroughly cleaned according to manufacturer's recommendations. The dosing pump accuracy should be checked under the same conditions. Generally, the PC Titrate should be kept clean and free of corrosive residues. The PC should be backed up on a regular basis to preserve data integrity. The tubing on the peristaltic pump will need to be changed periodically for proper functioning. Consult the manual for specific maintenance instructions. All maintenance must be recorded in the PC Titrate section of the General Chemistry Maintenance Log.

7.6 Analysis

7.6.1 All samples are initially analyzed by using the 0.02 N titrant.

7.6.2 Verify that the water reservoir is filled and the drain lines are properly positioned. The burret must be purged a total of 6 times, 3 times with DI water and another 3 with the titrant.

7.6.3 Place ~30 mLs of each standard, sample, buffer, and blank in labeled centrifuge tubes and place the tubes in order from back to front, left to right, in the autosampler. The alkalinity run must start with a pH calibration script (method).

Note: After the final pH 7.0 buffer (last PHC), park the probe in the last position on sample rack. The centrifuge, labeled storage, is filled with pH4 buffer and fluoride gases.

7.6.4 From the PC desktop, click on the MANTECH PRO icon, select ok when no user comes up and exit out of pop up window. Select the pH calibration shortcut or the shortcut tab.

7.6.5 The run template that appears can be edited by double clicking in each column (for position number and script). Make sure the vial position numbers in the template match. Note: if you need to edit the script or position; it can be done under the run table tab.

7.6.6 Click on "save template". Enter today's date under "enter search text", and then click on "OK".

7.6.7 Click on “check time table” and then “start”.

7.6.8 The instrument will first calibrate the pH meter, and then it will continue to the end of the run. The instrument will draw the correct volume of each sample or standard from the autosampler into the reaction vessel, where the titrant is then quantitatively added. The PC Titrate calculates and records the alkalinity result, in mg/L as $CaCO_3$, when it is electronically stable at each of the endpoints, when applicable. The time required may vary from sample to sample.

7.6.9 When evaluating the sample data, if a sample’s total Alkalinity result reads ‘0.00’ from the instrument, **FIRST** check the pH of the sample. If the pH is less than 4.5, the sample can be reported from the 0.02 N titrant analysis run. However, if the pH is greater than 4.5, then the sample will need to be re-analyzed using the stronger titrant of 0.1 N.

7.7 Documentation

7.7.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

7.7.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

7.7.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs are scanned and attached to the Documents section in the LIMS analytical batch.

7.7.4. Record all sample results and associated QC directly into LIMS. Level I and Level II reviews are performed in LIMS.

Examples of items included in the above reviews are as follows:

- QC data are outside the specified control limits for accuracy and precision
- Unusual detection limit changes are observed
- Samples having unusually high results
- Samples exceeding a known regulatory limit
- Raw data indicating some type of contamination or poor technique
- Transcription errors
- Results outside of calibration range
-

Notes:
Very high alkalinities may appear incorrectly on the instrument pages as non-detects. Review the results carefully. Any zero result for a sample with pH >4.5 must be reanalyzed using a higher normality titrant.

Because pH is a logarithmic scale, the acceptance limits are ± 0.2 SU (Standard Units). TALS is unable to evaluate or report ± limits; therefore, the ICV/CCVs are not reported from TALS.

8.0 QUALITY CONTROL

8.1 QC Summary

8.1.1 One MB and one LCS will be included in each laboratory lot of 20 or fewer samples. The MB will be examined to determine if contamination is being introduced in the laboratory. The LCS will be examined to determine accuracy of the method and cumulative LCS data will provide precision data.

8.1.2 Accuracy will be measured by the percent recovery (%) of the LCS. The recovery must be in range, as determined by in-house control limits or statistical analysis, in order to be considered acceptable. And, precision will be measured by the cumulative reproducibility of the LCSs.

8.1.3 The Method Duplicate, identified in TALS as DU, is performed per matrix per 20-sample analytical set, unless otherwise requested. Results must agree within the in-house precision limits or statistical control limits in order to be considered acceptable.

8.2 Corrective Actions

When an out-of-control situation occurs, the analysts must use his/her best analytical judgment and available resources to determine the corrective action to be taken. The out-of-control situation may be caused by more than one variable. The analyst should seek the assistance of his/her immediate supervisor, QA personnel, or other experienced staff if he/she is uncertain of the cause of the out-of-control situation. The test must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out of control situation should be reanalyzed. Out-of-control data must never be released without approval of the Supervisor, Project Manager, Technical Director, QA Manager or the Lab Director.

Listed below are steps that MUST be taken when an out-of-control situation occurs:

- demonstrate that all the problems creating the out of control situation were addressed;
- document the problem and the action which was taken to correct the problem with a Non-Conformance Memo (NCM) in TALS;
- receive approval (signature) of the Supervisor, Project Manager, Technical Director, QA Manager, or the Laboratory Director prior to the release of any analytical data associated with the problem.

Suggested Actions to specific out of control situations:

QC Indicator	Suggested Corrective Actions
ICV	• repeat the ICV to verify proper preparation; • pour fresh buffer; • check for instrument base-line drift; • re-calibrate with fresh buffers, reanalyze.

QC Indicator	Suggested Corrective Actions
LCS	• reanalyze LCS to verify that an out of control situation exists; • determine the source of error within the preparation procedure, correct the problem and repeat the sample set. (Sources of contamination could be the reagents, the LCS stock solution, or the preparation area.) • Non-detect samples may be reported if the LCS bias is high, but note out-of-control LCSs in a NCM.
MB	• Reanalyze the MB to verify that the contamination is at a level > Reporting Limit; • Determine the source of contamination and correct the problem; • all samples whose concentration is <10 times the MB level must be reprocessed and reanalyzed; any sample which is >10 times the MB level need not be reanalyzed. However, note out-of-control MBs in a NCM.
Matrix Duplicate (DU)	• the sample must be reprocessed and reanalyzed unless the sample concentration is <5 times the Reporting Limit, then the ± Reporting Limit rule applies; • if the reanalysis is within the control limits, the second value is reported; • if the reanalysis is still outside of the control limits, a CAR must be written and then approved by your Section Manager. • Note out-of-control DUs in a NCM.
CCV	• Repeat the CCV to verify a proper reading; • Pour a fresh CCV buffer; • Check for instrument base-line drift; • Recalibrate with a fresh buffers and repeat all samples since the previous in-control CCV; • Never dispose of any samples until you are sure that all QC are within their designated control limits.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 Normality of Titrant, N

$$\frac{A \times B}{53 \times C}$$

Where:
A = g Na_2CO_3 weighed into 1.0 L
B = mL Na_2CO_3 solution taken from titration
C = mL acid used to inflection point

This is only required when preparing titrant at the laboratory. Purchased titrant is certified by the manufacturer at a certain normality, given on the label.

9.2 Alkalinity: >20 mg/L as $CaCO_3$

$$\text{mg } CaCO_3/L \text{ (kg)} = \frac{A \times N \times 50000}{\text{mL or g of sample}}$$

Where:
A = mL standard acid used
N = Normality of standard acid (titrant)

The sample results are calculated by the PC Titrate software, based on 25 mL of sample volume, the volume of titrant added by the auto-titrator, and the normality of the titrant as entered by the analyst.

9.3 Alkalinity: <20 mg/L as $CaCO_3$

$$\text{mg } CaCO_3/L \text{ (kg)} = \frac{(2B - C) \times N \times 50000}{\text{mg or g of sample}}$$

Where:
B = mL titrant to 1st recorded pH
C = B + mL titrant to lower pH the additional 0.30 units
N = Normality of standard acid (titrant)

The additional low-level titration and this corrective calculation are done automatically by the PC Titrate software.

9.4 Converting Soil/Waste Results to Percent Alkalinity

$$\frac{\frac{mg}{kg}}{10000}$$

This calculation is done in TALS.

9.5 Accuracy

9.5.1 LCS % Recovery

$$\frac{\text{observed concentration}}{\text{actual concentration}} \times 100$$

9.6 Precision

9.6.1 DU Relative Percent Difference (RPD)

$$\frac{|\text{Orig.Sample Value} - \text{Dup.Sample Value}|}{\left[\frac{\text{Orig.Sample Value} + \text{Dup.Sample Value}}{2}\right]} \times 100$$

9.7 Alkalinity Relationships

The following discussion is included for explanatory purposes only. The PC Titrate provides the results for all alkalinity forms for all samples.

In addition to total alkalinity, calculation of alkalinity relationships is also possible. The results obtained for a phenolphthalein end point and the total alkalinity determination offers a stoichiometric classification of the three principle forms of alkalinity present in many waters. The classification ascribes the entire alkalinity to bicarbonate, carbonate and hydroxide, and assumes the absence of other (weak) inorganic or organic acids such as phosphoric and boric acids.

When alkalinity relationships are requested, the sample aliquot must first be titrated to an endpoint of pH 8.3. Record the titrant used. Then the titration is continued to pH 4.5. From the phenolphthalein alkalinity (to pH 8.3) and the total alkalinity, the various forms are calculated using the following table. Again, this is done for every sample by the PC Titrate. The analyst need only report what the client requests.

Relationship	Hydroxide Alkalinity	Carbonate Concentration	Bicarbonate Concentration
P = 0	< 5	< 5	T
P < 1/2 T	< 5	2P	T – 2P
P = 1/2 T	< 5	2P	< 5
P > 1/2 T	2P – T	2(T-P)	< 5
P = T	T	< 5	< 5

P = Phenolphthalein alkalinity (as $CaCO_3$ titrated to pH 8.3)
T = Total alkalinity (as $CaCO_3$ titrated to pH 4.

9.8 CO2 Calculations

The pH, Bicarbonate and Carbonate Alkalinity fields are obtained from the PC Titrate anlaysis,
based on the table in method SM2320B.

The Free and Total CO2 calculations are from method SM4500-CO_2 D which is completed in TALS

Free CO_2 = 2.0 X bicarb alk X $10^{(6\text{-}pH)}$

Total CO_2 = free CO_2 + 0.44 [(2(bicarb alk) + carb alk]

10.0 Pollution Control

It is Eurofins policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

10.1 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to UP-WM-001.

There are no special waste streams associated with this method.

- Waste from this procedure will enter the “Corrosive wastewater” wastestream.
- Single component standards will be turned over to the EHSC or Waste Technician.

11.0 METHOD PERFORMANCE CRITERIA

Refer to Sections 1, 6, 7, and 8.

12.0 REFERENCES

Refer to Section 1.0

13.0 ATTACHMENTS

N/A

14.0 REVISION HISTORY

- Revision 24 updated on 08/2/24
- Annual Review
- Throughout removed reference to data checklist and removed attachment
- Section 1.0 added reference to SM 2310 B- 2021
- Section 1.1.1 updated corporate SOP
- Section 4.0 updated instrument list
- Section 5.0 added 1N H_2SO_4 titrant
- Section 7.6 updated to current instrument

TITLE: Wet Chemistry
Cyanide (Total and Amenable)

Approvals (Signature/Date):

Paul Kolarczyk — 3-27-23 — Date
Supervisor, Wet Chemistry

Chris Hoham — 3/29/23 — Date
Env. Health & Safety Coor.

Nicole Berg — 3/27/23 — Date
Quality Assurance Manager

Ray Shock III — 3/27/23 — Date
Technical Director

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1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) is used to determine total and amenable cyanide in drinking, surface, and ground waters as well as solid matrices.

On occasion, clients request slight modifications to this SOP for non-drinking water samples. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP), authorized via laboratory signature approval, and mentioned in the data package's case narrative. **Note: Method modifications are not allowed for Drinking Water samples without prior written approval from the US EPA.**

This SOP was written using the following references:

A. Total Cyanide

Method SW-846 9010C is the principal method of distillation of cyanide samples. QuikChem Method 10-204-00-1-X, which has been approved by EPA for determination of cyanide in drinking and wastewaters by micro-distillation is also cited. Method EPA 335.4 is cited for colorimetric assay of ground, surface, drinking, and wastewaters. Soils and ground waters are analyzed according to method SW-846 9012B.The QC protocols outlined in 9012B are followed when those methods are quoted, unless superseded by a project QAPP.

Note: Samples that contain an oil matrix are to be prepped using the 9013A extraction procedure, which is not performed at the Eurofins Chicago laboratory.

B. Amenable Cyanide

Standard Method 4500CN_G provides the basis for the process to remove cyanide amenable to chlorination. Following chlorination, samples are analyzed as a total cyanide.

C. Free Cyanide

SW-846 9014 states that free cyanide may be determined by the colorimetric assay found in that method, without pre-distillation. Eurofins Chicago filters and matrix-matches water samples in preparation for free cyanide analysis, but samples are analyzed by method SW-846 9012B or EPA method 335.4.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL), referred to as the detection limit (DL) in NELAC, is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants" with additional details are provided in the Eurofins Corporate SOP, *CA-QS-006, Detection Limits* and the Eurofins Chicago SOP, *UP-QA-017, Method Detection Limit Studies.* MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; the MDL study will be performed and verified on an annual basis, verifying the Lower Limit of Quantitation (LLOQ) for the method.

An Instrument Detection Limit Study (IDL) is performed every six months.

1.1.2 Demonstration of Capability

Before the laboratory may institute a new method and begin reporting results, the laboratory shall confirm that it can properly operate the method. A demonstration of capability is performed whenever there is a change in instrument type, method or personnel. An Initial Demonstration of Capability (IDOC) must be thoroughly documented and approved by the Department Manager/Supervisor and QA Manager prior to independently analyzing client samples. All associated documentation must be retained in the QA Department and in the Analyst Training files. For additional details on the demonstration of capability procedures followed, refer to the laboratory SOP, *UP-QA-QAM, Quality Assurance Manual, Sections 19.4.2 and 19.4.3.*

1.1.3 Reporting Limits (LLOQ)

Reporting Limits (LLOQ) are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. The laboratory maintains reporting limits that are higher than the MDL. Wherever possible, reporting is limited to values approximately 3-5x the respective MDL to ensure confidence in the value reported.

Matrix	Reporting Limit
Waters	5 µg/L
Sediments/Soils/Wastes	0.24 mg/Kg (based on 0.25 g sample size)

Note: Reporting limits will vary depending on sample volume/size, dilution factors, dry weight reporting (soils/waste) and annual MDL determinations.

1.1.4 Definitions

Refer to Section 3.0 of the Laboratory's Quality Assurance Manual (UP-QA-QAM).

1.2 Summary of Method

Cyanide, as Hydrocyanic Acid (HCN), is released from cyanide complexes in an acidified sample by means of a reflux-distillation operation and is trapped in a sodium hydroxide solution. The cyanide concentration in the solution is then determined colorimetrically.

If samples are to be analyzed for cyanide amenable to chlorination, one portion is first chlorinated with calcium hypochlorite. This reaction decomposes the less rigorously bound forms of cyanide within the samples. Both the chlorinated and a non-chlorinated portion are then subjected to the above method and the difference is reported as amenable.

In the colorimetric procedure, the cyanide is converted to cyanogen chloride (CNCl) by reaction with Chloramine-T at a pH < 8. After this reaction is completed, color is formed by the addition of pyridine-barbituric acid. After color development, the sample is analyzed on a visible spectrophotometer at a wavelength of 570 nm.

Note: Free cyanide is matrix-matched and colored directly, without distillation.

2.0 INTERFERENCES

Note: Eurofins Chicago treats samples for interferences rather than using the method of standard additions.

- Sulfides may react with CN- to produce SCN-, which is not measured in this test and may adversely affect the colorimetric procedure. In order to comply with the USEPA Method Update Rule (MUR) of 3/12/07 all samples must be field tested for sulfide and treated if necessary prior to preservation with NaOH. See footnotes 5 and 6 of the MUR holding time and preservation specifics for instructions. However, all samples suspected of containing sulfide upon receipt must be tested. All samples that test positive for sulfide will be diluted prior to analysis.
- Nitrates and Nitrites can be a positive interference and are routinely removed by the addition of sulfamic acid solution prior to distillation for total cyanide.
- Chlorine is a negative interference. Samples must be tested in the field for chlorine and treated with ascorbic acid if positive. However, all water samples suspected of containing chlorine must be tested by placing a drop on a strip of potassium-iodide starch paper. A blue color indicates the need for treatment. Add a few crystals of ascorbic acid to the sample until a drop on the test paper produces no color. Then, add an additional ~0.2 g for each 250 mL sample.
- Thiocyanate will not be detected in these methods. If sulfite, thiosulfate, or thiocyanate is known to be present in a sample it is the client's responsibility to send the samples to a facility that can use an alternative method.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual, Lab Specific Addendum to the CSM, and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coat and closed-toe, nonabsorbent shoes are a minimum.

3.1 Specific Safety Concerns or Requirements

- Potassium cyanide and sodium cyanide will give off Hydrogen Cyanide (HCN) gas if combined with strong acids. Inhalation of CN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.
- Sodium Sulfide will form Hydrogen Sulfide (HS) gas if combined with strong acids. Inhalation of HS gas may be fatal.
- Be certain the heating blocks are turned off when not in use.
- Keep the instrument shield closed while instrument is in use to prevent injury, instrument damage, and stray light away from samples and detectors.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Barbituric Acid	Irritant	Not established	Limited information. Inhalation may irritate respiratory tract. Causes skin and eye irritation. Should be treated as potential health hazard; do not ingest.
Hydrochloric Acid	Corrosive Poison	5 ppm – Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Cyanide	Poison Corrosive	5 mg/m^3 TWA as CN	**This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death.** Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heart beat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.
Pyridine	Flammable Irritant	5 ppm-TWA	Inhalation causes severe irritation to the respiratory tract. Symptoms of overexposure include headache, dizziness, nausea, and shortness of breath. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. Absorption through the skin may occur, resulting in toxic effects similar to inhalation. May act as a photosensitizer. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
Sodium Cyanide	Poison Corrosive	5 mg/m^3 TWA as CN (skin)	**This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death.** Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heartbeat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Silver Nitrate	Corrosive Poison	0.01 mg/m^3 (TWA)	This is a corrosive, poisonous material. It will cause burns to any area of contact and is harmful if inhaled. Ingestion may cause death. Contact with other material may cause fire.
Sodium Sulfide	Corrosive	10 ppm-TWA 15 ppm-STEL	Will form Hydrogen Sulfide (HS) gas if combined with strong acids. Inhalation of HS gas may be fatal. Symptoms include painful conjunctivitis, headache, nausea, dizziness, coughing and, in extreme cases, pulmonary edema and possible death. Irritant. Contact with skin can produce serious caustic burns with painful inflammation and possible destruction of tissue. Inflammation, tearing and pain may be expected. Severe contact can cause destruction of tissue.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 EQUIPMENT AND SUPPLIES

4.1 Spectrophotometer

- rAPID-T semi-automated spectrophotometer, capable of measuring at 570.0 nm
- Software – rAPID-T (Astoria Pacific Inc.) 1.3.3.5
- Cuvettes

4.2 Distillation Supplies

- SimpleDist Micro CN tubes by Environmental Express, or equivalent. Note: The 6 mL tube volume is verified per lot and is documented using the spreadsheet located in the W\QC\Wet Chemistry\Eppendorf_Verificaton_Check_Year directory.
- SimpleDist Micro heating blocks by Environmental Express, or equivalent (Note: Temperature verification against an NIST Thermometer is required on an annual basis)
- Press for sealing SimpleDist Micro tubes
- Eppendorf and volumetric pipettes

4.3 Miscellaneous

- Stir plate/stir bars
- Fume hood
- Vortex mixer
- General laboratory glassware
- Class A graduated cylinders and volumetric flasks, various sizes

5.0 REAGENTS AND STANDARDS

All reagents are prepared with Type II Deionized Water, unless otherwise specified, in Class A volumetric flasks. Chemicals must be reagent grade and ACS compliant.

All liquid reagents in glass containers must be stored in secondary containment.

5.1 CN Stock 1&2, 1000 mg/L

Stock 1 and Stock 2 are purchased as a certified standard from separate, reputable manufacturers. Certificates of Analysis must be on file for all purchased stocks.

Alternatively, reagents may be made in the laboratory using neat chemicals. Using an analytical balance capable of reading 0.1 mg, weigh 2.51 g Analytical Reagent Grade Potassium Cyanide (KCN) and 2.0 g Sodium Hydroxide (NaOH) pellets into a 1.0 L volumetric flask. Dilute to volume with DI water. Stocks made in-house from salt must be standardized. See section 6.1.

- Life of Reagent: 6 months or manufacturer's recommendation.
- Storage Requirements: Refrigerate in a plastic bottle

5.2 CN Working Standard I (WSI)

Dilute 1.0 mL of Stock Solution 1 to 100 mL in a volumetric flask with DI water.

- Life of Reagent: 2 weeks
- Storage Requirements: None

5.3 CN Working Standard II (WSII)

Dilute 1.0 mL of Stock Solution 2 to 100 mL in a volumetric flask with DI water.

- Life of Reagent: 2 weeks
- Storage Requirements: None

5.4 Hengar Granules or Ottawa Sand

Solid material to be used a matrix for batch QC (MB and LCS), purchased from vendor.

5.5 Calibration Verification and Quality Control Preparation

5.5.1 Distilled QC Stds

QC Standard	Standard Used	Standard Vol (mL)	Water Vol (mL)	Final conc (mg/L)
MB	--	--	6	---
LCS/ICV	WSII	0.100	9.9	0.100
MS/MSD	WSII	0.060	6*	0.100

*MS/MSD use 6 mL of sample instead of water; solids use 0.25g sample + 5 mL water

5.5.2 Undistilled QC Standards for Free Cyanide

QC Standard	Standard Used	Standard Vol (mL)	0.25 N NaOH Vol (mL)	50% NaOH Vol (mL)	Final conc (mg/L)
MB	--	--	Fill cup**	--	--
LCS/ICV	2nd Source Working (0.1 mg/L)	Fill cup**	--	--	0.1
MS	2nd Source Working (10 mg/L)	0.1	25*	0.5/0.3*	0.04

*Add 50% NaOH to 25 mL of sample: 500 µL if unpreserved, 300 µL if preserved
**Samples and QC are poured into a sample cup for analysis, non-critical volume.

5.5.3 QC Standards for Initial and Continuing Calibration

QC Standard	Standard Used	Standard Vol (mL)	0.25N NaOH Vol (mL)	Final conc (mg/L)
ICV	WSII	0.100	9.9	0.100
CCV	WSI	0.150	9.85	0.150
ICB/CCB	--	--	6	--
MRL	WSI	0.050	100	0.005

5.6 Cyanide Releasing Reagent

Dissolve 80.5 g Magnesium Chloride hexahydrate in 267g (or mL) DI water. Slowly add 368g concentrated sulfuric acid (~200mL). Add acid in a fume to avoid toxic fumes. Once the solution has cooled, it will yield approximately 500 mL.

- Life of Reagent: 6 months
- Storage Requirements: None

5.7 Chloramine-T

Dissolve 0.4 g Chloramine-T in a 100 mL volumetric flask with DI water. Dilute to volume with DI water.

- Life of Reagent: 1 week
- Storage Requirements: Refrigerate until ready to use.

5.8 Pyridine-Barbituric Acid

This reagent may be purchased as a pre-mixed solution or prepared in the lab as follows:

Under an exhaust hood, add 75 mL Pyridine to a 1.0 L volumetric flask with a large stir bar. Mix the solution on high and slowly add 15 g barbituric acid to avoid clumping. Allow this mixture to stir on a stir plate for ~15 minutes or until the barbituric acid is in solution. Add 15 mL concentrated Hydrochloric Acid (HCl) very slowly and allow the fumes to dissipate between additions. Dilute to volume with DI water. **CAUTION:** Flammable.

- Life of Reagent: 6 months
- Storage Requirements: Refrigerate

5.9 Sodium Phosphate Buffer

This reagent may be commercially purchased.

Dissolve 138 g of Sodium Phosphate Monobasic Monohydrate ($NaH_2PO_4 \cdot H_2O$) in a 1.0 L volumetric flask with DI water. Dilute to volume with DI water.

- Life of Reagent: 1 year
- Storage Requirements: Refrigerate

5.10 Lead Acetate Paper

Purchased from a chemical vendor.

- Life of Reagent: Manufacturers recommendation
- Storage Requirements: None

5.11 0.75 N Sodium Hydroxide

This reagent is purchased in bulk. It may also be made in the lab as follows:

Dissolve 300.0 g sodium hydroxide pellets in DI water and dilute to 1.0 L. It is convenient to make this reagent in 2-L volumetric flasks by using 60.0 g of NaOH. This reagent is used for both the Cyanide and Sulfide tests.

- Life of Reagent: 1 year
- Storage Requirements: None

5.12 ~1.25 N Sodium Hydroxide

Dissolve ~50 g sodium hydroxide pellets in DI water and dilute to 1 L. This reagent is used for pH adjustment during the chlorination step for amenable cyanide.

- Life of Reagent: Indefinite
- Storage Requirements: None

5.13 Sulfamic Acid Solution

Dissolve 10 g of sulfamic acid (H_2NSO_3H) to 100m L with DI water in a volumetric flask.

- Life of Reagent: 1 year
- Storage Requirements: None

5.14 Calcium Hypochlorite Solution, 0.35 M

Dissolve 5.0 g of calcium hypochlorite [$Ca(OCl)_2$] to 100 mL in a volumetric flask. Shake before using, but be sure to release the pressure caused by agitation while shaking.

- Life of Reagent: 1 Month
- Storage Requirement: Amber glass bottle

5.15 Hydrogen Peroxide 3% (H_2O_2)

Hydrogen peroxide 30% is purchase from a chemical vendor for metals digestion. This solution is diluted 10 mL to 100 mL in volumetric glassware.

- Life of Reagent: 6 months
- Storage Requirement: None

5.16 Potassium-Iodide Starch Test Paper

Purchased from a chemical vendor.

- Life of Reagent: Manufacturer's recommendation
- Storage Requirements: None

5.17 Silver Nitrate Titrant, 0.0192 N

Purchased NIST-traceable titrant from chemical vendor (1 mL = 1 mg cyanide). This reagent is available to standardize cyanide standards when required.

- Life of Reagent: 1 year
- Storage Requirements: Store in an amber bottle

5.18 Rhodanine Indicator

Dissolve 20 mg of p-dimethylaminobenzalrhodamine in 100 mL of acetone. This reagent is available to standardize cyanide standards when required.

- Life of Reagent: 1 year
- Storage Requirements: None

5.19 Bismuth Nitrate Solution, 0.062 M

Dissolve 30 g of bismuth nitrate ($BiNO_3 \cdot 5H_2O$) in ~100 mL DI water in a 1.0 L volumetric flask. While stirring, add 250 mL of glacial acetic acid (CH_3CO_2H), stir until dissolved. Dilute to 1.0 L with DI water.

- Life of Reagent: 1 year
- Storage Requirements: None

6.0 CALIBRATION

6.1 Standard Curve

The calibration curve points are prepared manually.

Standard (µg/L)	Source Standard (mg/L)	Volume of Source Standard (µL)	Volume of distilled blank (µL)
250	0.25	1000	0
100	0.25	400	600
50	0.25	200	800
25	0.25	100	900
5	0.25	20	980
2	0.05	40	960
0	--	1000	0

*Samples are diluted with distilled calibration blank.

Note: A diluter check will be performed on a quarterly basis to verify that the instrument is accurately performing dilutions. Acceptance limits are +/- 2.5%, the verification will be recorded in the maintenance logbook.

6.2 Standard Curve (Manual Preparation)

Standardization of Stock Standards: This procedure is included for availability, but is not routinely used since stock standards are purchased.

Pipette 25 mL of Stock Standard to a 300 mL Erlenmeyer flask. Add 0.5 mL of Rhodanine Indicator to the solution. Titrate with standard silver nitrate titrant to the change in color from a canary yellow to a salmon hue. Titrate a blank containing 25 mL of 0.25 N sodium hydroxide. Use the calculation below:

$$mg\frac{CN}{L} = \frac{(A-B)\ X\ 1000}{25\ mL}$$

Where:
A = mL $AgNO_3$ used for standard solution

B = mL $AgNO_3$ used for blank
Using the average concentration obtained from 3 titrations, calculate and add the amount of DI Water required to adjust the concentration to exactly 1000 mg/L. Titrate as above to verify that the concentration is 1000 ± 5 mg/L. Re-adjust and re-titrate if necessary.

7.0 PROCEDURE

7.1 Quality Control Limits/ Analytical Sequence

Quality Control Item	Frequency	Acceptance Limits
Calibration Curve (Linear – 1st Order)	Daily prior to samples	r ≥ 0.995; Standard read-back ± 10% y-intercept < abs. value of RL
ICV (Initial Calibration Verification)	Immediately after curve	85 – 115% 9012B 90 - 110% 335.4
ICB (Initial Calibration Blank)	After ICV	< Reporting Limit (RL)[1] <1/2 RL (per QAPP)
CCV (Cont. Calibration Verification)	After every ≤ 10 readings and after last sample reading	90 - 110%
Lab Control Sample (LCS)	1 / set of ≤ 20 samples	85 - 115% for 9012B 90 - 110% for 335.4
CCB (Cont. Calibration Blank)	After every CCV	< RL <1/2 RL (per QAPP)
Method Blank (MB)[2]	1 / set of ≤ 20 samples	< RL <1/2 RL (per QAPP) < MDL (Drinking Waters)
Matrix Duplicate (DU) (MS/MSD may be used for precision.)	Per QAPP / Project	≤ 20 RPD
Matrix Spike (MS) (MSD if required per QAPP/Project)	1 / set of ≤ 10 samples	75 - 125% for 9012B 90 - 110% for 335.4
Method Reporting Limit (MRL)	Per QAPP / Project	70 - 130%

[1] The NELAC document refer to the RL as the Limit of Quantitation (LOQ)
[2] A chlorine-treated MB for amenable cyanide must be prepared when amenable cyanide is done.
Note: Drinking Water (DW) samples must be done in sets of 10 or fewer samples rather than 20.
Note: When QC requirements are specified in client specific QAPPs, they supersede the above table.

7.2 Sample Preservation and Storage

All samples must be stored at 4 ± 2°C. All aqueous samples must be preserved with NaOH to a pH >12. Solid and non-aqueous samples are not chemically preserved.

Sample container, preservation technique and holding time may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client request. Listed below are the holding times, and references that include container and preservation requirements.

Regulation	Holding Time	Preservation[1]	Reference
CWA	14 days from collection	NaOH, pH > 12	40 CFR Part 136[2]
SDWA	14 days from collection	NaOH, pH > 12	40 CFR Part 136
RCRA	14 days from collection	NaOH, pH > 12	SW-846, Updates 3 & 4

[1]Samples are to be preserved with 2 mL 10 N NaOH/L (+ 0.6 g ascorbic acid/L in chlorinated water source). The holding time for chlorinated samples preserved with ascorbic acid is 24 hours.

[2]The CWA and SDWA preservation requirements were enhanced as part of the MUR on 3/12/07. Requirements for on-site testing and treating for sulfide were added and described.

7.3 Sample Preparation

7.3.1 Sample Sizes

Matrix	Sample Size
Waters - total	6 mL
Waters - amenable	50 mL
Waters - free	25 mL
Sediments/Soils/Wastes	0.25 g

7.3.2 Pre-Test for Sulfide

All samples must be pretested for the presence of sulfides. This is done by placing lead acetate paper onto a paper towel on the bench and pipetting 1-2 drops of the sample onto the test paper when transferring the sample with a pipette to the sample tube. A positive test is indicated by a brown or black color on the paper.

In sample preparation, it is required that all samples are treated with bismuth nitrate and sulfamic acid solution. If sulfide is found to be present within a sample, it would be removed during these steps in the preparation process.

7.3.3 Sample Preparation - Total Cyanide

7.3.3.1 Turn on the SimpleDist Micro hot block. The block must be set at 120°C and takes about 30 minutes to heat up.

7.3.3.2 Add 2 mL of 0.75N NaOH solution to the M (Measurement) end of the collector tube. Place a membrane and cap on the collection tube, making sure the membrane completely covers the tube after assembly. A sample batch label may be placed upside down on the upper part of the tube near the breakaway point.

7.3.3.3 For aqueous samples add 6 mL of sample to the sample tube. For solids and non-aqueous liquids add 0.25g of sample and 5 mL water to the sample tube. Record the sample weights into a TALS preparation batch. Do not place labels on the sample tube, or they will melt and ruin the hot block.

7.3.3.4 Use Hengar granules as a matrix for solid QC samples.

7.3.3.5 Spike MS/MSD with 0.06mL of 1 ppm standard.

7.3.3.6 Add 0.100mL bismuth nitrate solution to each sample tube

7.3.3.7 Add 0.25mL sulfamic acid solution to each sample tube.

7.3.3.8 Add 0.75mL cyanide releasing agent and immediately assemble tube, using the tube press.

7.3.3.9 Once all tubes are completely assembled, insert them into the hot block, making sure they are all the way to the bottom.

7.3.3.10 Allow the tubes to cook for 30 minutes. Do not remove a tube to check on it during the cooking time, as it will ruin the sample. (Note: This is a method modification from 335.4.)

7.3.3.11 At the end of the cook time, individually remove and invert each tube so that the cap is at the bottom. Immediately separate the sample tube from the collection tube. Failure to separate these parts within 4 seconds will result in suck back into the sample tube and sample loss.

7.3.3.12 Once cooled, about 30-45 minutes, the distillate may be rolled around the inside to collect all of the small droplets. Firmly grasp both sides of the tube and snap it in half.

7.3.3.13 Samples are brought up to the 6 mL mark with DI water. Samples may be analyzed immediately, or covered with parafilm if analysis will happen later.

Note: Analysis must be performed within a day of preparing samples.

7.3.3.14 Refer to Section 7.6 for quantitative determination of cyanide in the solution.

7.3.4 Sample Preparation - Amenable Cyanide

NOTE: Treatment for Amenable Cyanide must be done in Ray-Guard UV blocking Erlenmeyer flasks, or in flasks that are completely covered with aluminum foil to block UV light.

7.3.4.1 The sample is first analyzed for total cyanide, if the sample is non-detect, the treatment step is unnecessary and the amenable cyanide can be reported as non-detect based on the total cyanide non-detect result, an NCM is written when this occurs.

If total cyanide is detected, use a second 50 mL sample aliquot or a volume diluted to 50 mL, add calcium hypochlorite solution dropwise while agitating and maintaining the pH between 11 and 12 with 1.25 N sodium hydroxide.

The initial reactive product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, this reaction must be performed in a hood.

For convenience, the sample may be agitated in a 500 mL Ray-Guard Erlenmeyer flask by means of a magnetic stirring device.

Note: The total cyanide LCS is processed with the amenable cyanide samples and analyzed. This result is updated in the non-amenable batch in TALs. The non-amenable cyanide result is subtracted from the total cyanide LCS result in the cyanide amenable calculation batch.

The LCS is calculated as an amenable to chlorination LCS with a control limit of 90-110% (335.4) and 85-115% (9012B).

7.3.4.2 Test for residual chlorine with Potassium Iodine (KI)-starch paper and for pH with test strips at least every 15 minutes and maintain this excess for one hour, continuing agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional calcium hypochlorite solution any time during the hour. The analyst needs to record that this monitoring was done in the batch.

7.3.4.3 After one hour, add 8 drops H_2O_2 followed by 4 drops $Na_2S_2O_3$ solution (500 g/L) to destroy excess chlorine. Test with KI-starch paper to verify that no chlorine is present.

7.3.4.4 Transfer 6 mL of the treated aliquot to a SimpleDist Micro tube and distill as total cyanide samples.

NOTE: In matrices high in nitrates, CN can actually be formed during the chlorination process, resulting in a higher concentration after chlorination than was measured before and a negative value for amenable CN. This may be prevented by adding sulfamic acid to the sample before adding the chlorine during the treatment. A Non-Conformance Memo (NCM) is required when this occurs.

7.3.6 Sample Preparation – Free Cyanide

Add 500 µL of 50% NaOH to 25 mL of filtered aqueous samples and stir until dissolved. Use 300 µL of 50% NaOH for preserved samples. The NaOH concentration is critical for successful color development, and must match the 0.25 N NaOH that the standards and blanks are made with. Transfer an aliquot of the basic solution to an instrument sample cup for direct analysis without distillation.

7.4 Calibration / Standardization

Before any instrument is used as a measurement device, the instrumental response to known reference materials must be determined. The manner in which various instruments are calibrated is dependent on the particular type of instrument and its intended use. All sample measurements are made within the calibrated range of the instrument. Preparation of all reference materials used for calibration will be documented.

Instrument calibration consists of two types: Initial Calibration and Continuing Calibration. Initial Calibration procedures establish the calibration range of the instrument and determine the instrument response over that range. Continuing Calibration is used within the analytical sequence to verify stable calibration throughout the sequence, and/or to demonstrate that instrument response did not drift during a period of non-use of the instrument. Refer to the Eurofins Corporate Policy, NDSC-QA-QP44940, *Calibration Curves and the Selection of Calibration Points* and the *Calibration Criteria Training, Inorganics* Document CHI-22-09-472 for further guidance.

7.5 Preventive Maintenance

- Wipe any reagent spills from all instrument surfaces as soon as possible.
- Be sure to run the end of day program on the rAPID-T daily to clean sample pathways.

7.6 Sample Analysis

7.6.1 Turn on the rAPID-T and allow it to warm up for 30 minutes prior to use. Run the start of day program.

7.6.2 Make sure there are no air bubbles in the syringe. If bubbles are present, use ethanol or propanol to dislodge them. Substitute a beaker of alcohol for the rinse water and prime the syringe 5 or more times. If this doesn't work, remove the syringe and manually flush with alcohol to remove all air bubbles. Prime the syringe 5 or more times with water to remove the alcohol from the system.

7.6.3 The instrument will automatically select the most recently used method. Be sure to verify that the correct method is selected.

7.6.4 Fill all reagents to the neck of the bottle and place in the appropriate location of the instrument. Be sure to make sure there are new cuvettes in the rack and clear the cuvette rack in the software.

7.6.5 Pour sufficient sample into cups and place in the instrument. A single CCV and CCB cup may be filled and used throughout the run. Analyze a CCV/CCB pair at the start of each day, after every ten samples, and at the end of the run. A CCV/CCB pair is not needed if samples are analyzed immediately following an initial calibration.

7.6.6 Scan samples and QC to the instrument queue and start the instrument.

7.6.7 At the end of the run the calibration and results are printed. Results are also exported to TALS. From the File menu select Export, then Data File. Click the folder icon by the destination and select either 9012B for total results or 9012B_NonAmen for non-amenable cyanide results. Amenable Cyanide results are calculated via 9012B_Calc batches after the total and non-amenable cyanide results are obtained.

7.7 Documentation

All data is entered into TALS. Ensure that the digestion times and date and the Standard IDs are recorded and correct.

7.7.1 TALS Entry

Both water samples and soil samples require a preparation batch and an analytical batch in TALS ADII for cyanide. Sample IDs from the original containers are scanned directly into the prep batch. When distillation is complete, the bar codes of the secondary container IDs generated on a print-out from the preparation batch are scanned into the rAPID-T software.

7.7.2 Traceability of Standards

Upon receipt or preparation, each standard and reagent is entered into the reagent module in TALS (the laboratory's LIMS) and is issued a unique ID#. Further information as applicable is entered into TALS including the manufacturer; lot #; the date received or prepared; the expiration date; volume/weight received; concentration; preparation details; recording analyst; and the description of the item (e.g., Cyanide Stock 2 - 1000 ppm). Once the record is created, a unique label is printed and affixed to the appropriate standard/reagent container. Biweekly intermediate standards are similarly entered into the reagent module and labeled. The volume of intermediate standards required in the final working standards are entered into the ADII batches along with the TALS codes so that the final working concentrations can be calculated.

7.7.3 Data Review

Analytical data goes through a 200% review cycle. As results are generated, analysts review their work to ensure that the results generated meet QC requirements and relevant EPA methodologies. The analyst transfers the data into TALs in the Analyst Desktop module. Where non-compliance is observed, the analyst creates Non-Conformance Memos (NCMs) in TALs. Flags and data qualifiers can be method, project, program or QAPP specific. The analyst documents the initial review in AD batch and sets the status in LIMs to 1st level review. The second level or peer review of the data is conducted by another individual who has been trained on the review process. This secondary review is documented in the batch, making any necessary corrections to the data or additions to the NCMs as necessary. The batch is then set to 2nd level review. The raw data, including the instrument print-outs and manual entries, and electronic files

are retained for easy retrieval in accordance with the laboratory's record and retention policy outlined in the SOP, *UP-QA-QAM, Section 16*.

Examples of items included in the above reviews are as follows:

- QC data are outside the specified control limits for accuracy and precision
- Unusual detection limit changes are observed
- Samples having unusually high results
- Samples exceeding a known regulatory limit
- Raw data indicating some type of contamination or poor technique
- Transcription errors
- Results outside of calibration range

8.0 QUALITY CONTROL

8.1 QC Summary

NOTE: Internal statistical limits are available on a client-or project-specific basis.

8.1.1 One MB and one LCS will be included in each laboratory lot of 20 or fewer samples (10 for DW sets). The LCS and MBs will be in an aqueous media for all methods unless specified in a client Quality Assurance Plan QAP). MBs and LCSs must be distilled with the sample set.

8.1.2 The MB will be examined to determine if contamination is being introduced in the laboratory.

8.1.3 The LCS – when performed in duplicate as required by the client and/or contract – can be examined to determine both precision and accuracy.

8.1.4 Accuracy will be measured by the percent recovery (%R) of the LCS. The recovery must be in range, as determined by appropriate control limits, in order to be considered acceptable. Additionally, %R will be plotted on control charts to monitor method accuracy.

8.1.5 Precision can be measured by the reproducibility of both LCS's (when performed in duplicate – see Section 8.1.3) and will be calculated as relative percent difference (RPD). Results must agree within appropriate control limits in order to be considered acceptable.

8.1.6 One MS and MSD are done per matrix per 10-sample analytical set. Results must agree within the default precision/accuracy limits, method limits, statistical control limits, or other, client-specified limits in order to be considered acceptable.

8.2 Corrective Actions

When an out-of-control situation occurs, the analysts must use his/her best analytical judgment and available resources to determine the corrective action to be taken. The out- of-control situation may be caused by more than one variable. The analyst should seek the assistance of his/her immediate supervisor, QA personnel, or other experienced staff if he/she is uncertain of the cause of the out-of-control situation. The analysis must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out-of-control situation should be reanalyzed. Out-of-control data must never be released without approval of the supervisor, project manager, QA personnel or the laboratory manager.

Listed below are steps that MUST be taken when an out of control situation occurs:

- demonstrate that all the problems creating the out of control situation were addressed;
- document the problem and the action which was taken to correct the problem on the data review checklist;
- document on the checklist that an in-control has been achieved; and
- receive approval (signature) of the supervisor, Project Manger, QA personnel, or the Laboratory Manager prior to the release of any analytical data associated with the problem.

Suggested Actions to specific out of control situations:

8.2.1 Calibration Curve

- reanalyze the standard curve;
- prepare new stock and/or working standards;
- check reagents/solutions and prepare fresh if necessary.
- The high point of the calibration curve may be turned off, provided there are enough data points to meet criteria and the linear range of reported data is adjusted. A new curve must be prepared when any of the standards does not meet criteria or the “r” value is <0.995.

8.2.2 Initial Calibration Verification (ICV)

- repeat the ICV to verify its proper preparation;
- prepare a new ICV from the original stock;
- check for instrument base-line drift;
- re-standardize with existing standards, reanalyze;
- check reagents/solutions and prepare fresh if necessary;
- prepare new stock and/or working standards and recalibrate.

8.2.3 Initial Calibration Blank (ICB)

- prepare a new ICB to verify proper preparation;
- verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc., to achieve stability;
- determine the source of contamination by the process of elimination, correct the problem and reanalyze. (Carry over from a previous analysis and reagent contamination are two common sources).

8.2.4 Laboratory Control Standards (LCS)

- re-read the LCS to verify that an out-of-control situation exists;
- determine the source of error within the preparation or analysis procedures, correct the problem and repeat the sample set. (Sources of contamination could be from the reagents, the LCS stock solution, or the preparation area.)

Precision: When performed in duplicate, the LCS and LCD must meet the control limits of $\leq$ 20 RPD. If these criteria are not met and both LCS's meet the % Recovery control limits, then see your supervisor or the Inorganics Manager for proper corrective action.

8.2.5 Method Blank (MB)

- re-read the MB to verify the contamination at a level > Reporting Limit;
- determine the source of contamination and correct the problem;
- all samples whose concentration is detected at <10 times the MB level must be reprocessed and reanalyzed;

- any sample which is >10 times the MB level need not be reanalyzed; however, document the situation on the data review checklist and have it approved prior to the reporting of the data.

8.2.6 Sample Duplicate (DU)

- the sample must be reprocessed and reanalyzed unless the sample concentration is <5 times the Reporting Limit, then the ± Reporting Limit rule applies;
- if the reanalysis is within the control limits, the second value is reported;
- Note out-of-control DUs on the data review checklist which must be approved by the Supervisor or Inorganics Manager.

8.2.7 Matrix Spike (MS)

- When a single spike is out of control, it must be reprocessed and reanalyzed unless the sample concentration exceeds the spike concentration by a factor of 4 times; CLP requires only a post spike on the sample distillate when a distilled spike is outside acceptance limits. Report all spikes, whether or not they are in control.

8.2.8 Continuing Calibration Verification (CCV)

- repeat the CCV to verify proper preparation;
- prepare a new CCV from original stock;
- check for instrument base-line drift;
- check reagents/solutions and prepare fresh if necessary;
- recalibrate with a new standard curve and repeat all samples since the previous in control CCV;
- never dispose of any samples until you are sure that all QC are within their designated control limits.
- all reported data must be bracketed by in-control CCVs/CCBs. If a CCV is outside the limits, all readings taken on either side of that CCV must be re-read, regardless of the cause and resolution of the out-of-control situation.

8.2.9 Continuing Calibration Blank (CCB)

- prepare a new CCB to verify proper preparation;
- verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc. to achieve stability;
- determine the source of contamination by the process of elimination, correct the problem and reanalyze all the samples since the previous in control CCB. (Carry over from a previous analysis and reagent contamination are two common sources).
- never dispose of any samples until you are sure that all QC are within their designated control limits.

9.0 Data Analysis and Calculations

9.1 Calculation of Water Samples

The rAPID-T instrument will calculate the final result in mg/L, provided dilutes are entered into the rAPID-T sample queue. Manual dilutions are entered into the “manual” column and requested instrument dilutions are entered into the “pre-dilution” column. The “manual” dilution consists of dilution of the final distillate immediately prior to placing onto the instrument. If a lower sample

volume is used during the preparation of the sample, prior to distillation, the actual volumes used should be recorded in TALS only and not be included in the "manual" dilution column of the instrument. The instrument may also perform additional dilutions when a sample exceeds the calibration range. The total product of all dilutions is summarized in the final results table. The final result provided by the instrument includes all dilution factors.

The measured instrument absorbance is used to calculate concentration, C (mg/L), of each sample using the calibration curve.

$$Final\ Result\ \left(\frac{mg}{L}\right) = \frac{C\ \left(\frac{mg}{L}\right) X\ Dilution\ Factor\ X\ final\ sample\ volume\ (mL)}{initial\ sample\ volume}$$

Water samples typically use a 6 mL initial and final volume, which simplifies this equation to:

Final result (mg/L) = C(mg/L) x Dilution factor

9.2 Calculation of Soil/Sediment/Waste Samples

Solid results are calculated in a similar fashion to water samples; however, the final calculation will always need to account for a variable initial sample volume. The typical sample volumes for solids are an initial sample volume of 0.25g and a final volume of 6mL.

$$Final\ Result\ \left(\frac{mg}{Kg}\right) = \frac{C\ \left(\frac{mg}{L}\right) X\ Dilution\ Factor\ X\ final\ sample\ volume\ (mL)}{initial\ sample\ volume\ (g)}$$

Sample results may be corrected to report on a dry weight basis:

Final result, dry weight corrected (mg/Kg) =

$$\frac{Final\ result\ above\ \left(\frac{mg}{Kg}\right)}{\%\ total\ solids}$$

NOTE: All dry weight corrections are made in TALS at the time of data entry. The final result will not calculate unless the % solids result is at second level review.

9.3 Calculation of Amenable Cyanide

Amenable Cyanide = Total Cyanide – Non-Amenable Cyanide

Total (9012B) and non-amenable (9012B_Non-amen) cyanide results are uploaded into separate TALS batches. The difference is calculated by TALS in the 9012B_Calc batch.

9.4 Accuracy

9.4.1 ICV/CCV, LCS/LCD % Recoveries

$$\%R = \frac{ovserved\ concentration}{acutal\ concentration}\ X\ 100$$

9.4.2 Matrix Spike % Recovery

$$\%R = \frac{(spiked\ concentration) - (unspiked\ concentration)}{spike\ concentration}\ X\ 100$$

9.5 Precision

9.5.1 DU, MSD, and LCSD Relative Percent Difference (RPD)

$$RPD = \frac{|orig.sample\ value - dup.sample\ vaule|}{[\frac{orig.sample\ value + dup.sample\ value}{2}]}\ X\ 100$$

9.6 Reporting Results

Without rounding, enter the raw data into the TALS. See section 7.7.3 for data handling.

10.0 Pollution Control

It is Eurofins policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

10.1 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to UP-WM-001.

The following waste streams are produced when this method is carried out.

- Wastewater contaminated with Pyridine. Waste will be collected in approved containers and poured into the carboy labeled Pyridine and Water using a funnel to reduce splashing.
- Alkaline distillate waste remaining in scrubbers will be collected in approved containers and poured into the carboy labeled Corrosive Wastewater.
- Autosampler rinse waste will be collected in approved containers and poured into the carboy labeled Corrosive Waste Water.
- Alcohol used for syringe cleaning will be poured into the carboy labeled Flammable Waste.

11.0 Method Performance Criteria

Refer to Sections 1, 6, 7 and 8.

12.0 REFERENCES

Refer to Section 1.0.

13.0 ATTACHMENTS

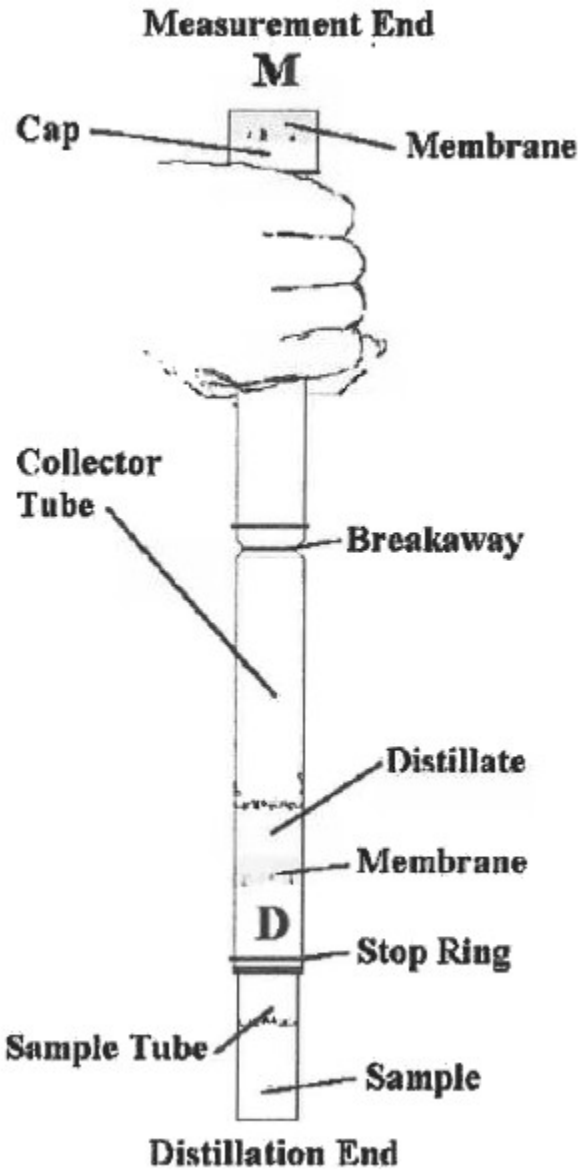
Figure 1. Example: SimpleDist Micro distillation tube

14.0 REVISION HISTORY

- Revision 04 updated on 03/27/23
- Annual Review
- Sections 5.2 and 5.3 High and Low Level Working Standards were replaced with WSI and WSII.
- Sections 5.4 and 5.5 were removed.
- Sections 5.5.1 and 5.7.3 tables were updated with new standards, volumes, and concentrations.
- Section 5.5.1 LLCS and HLCS were removed from the table.
- Section 5.9 was updated to adjust the life of the reagent.
- Section 5.13 preparation and concentration for a NaOH solution was updated.
- Section 5.21 was removed.
- Section 6.1 the calibration curve is prepared manually and the table was updated with a new source standard and dilutions according to the standard.
- Section 7.1 LLCS and HLCS were removed from the table
- Section 7.2.2 intermediate standards were updated to be prepared biweekly instead of daily.
- Section 7.3 was updated regarding the pre-test instructions for sulfide.
- Section 7.3.3.2 was updated to include the new concentration of the NaOH solution.
- Section 7.3.3.5 was updated with the current MS/MSD spike measurements.
- Section 7.3.3.6 instructions for adding Bismuth Nitrate solution to each tubes was inserted, shifting all remaining sections in 7.3.3 down.
- Section 7.3.3.11 instructions for inverting the sample tube were moved to Section 7.3.3.10
- Section 7.3.3.12 requirement for samples to be ran within a day were specified.
- Section 7.4 the corporate policy method reference was updated.
- Sections 8.1.7 and 8.2.10 were removed.

Figure 1.

Example: SimpleDist Micro Distillation Tube (023-001)



TITLE: WET CHEMISTRY
Total Ammonia, Unionized Ammonia and Ammonium Ion
Automated Phenate Method

Approvals (Signature/Date):

Paul Kolarczyk 4-16-24
Paul Kolarczyk Date
Supervisor, Wet Chemistry

Chris Hoham 4/16/24
Chris Hoham Date
Environmental Health & Safety Coor

Nicole Berg 4/16/24
Nicole Berg Date
Quality Assurance Manager

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1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) is used to determine the total and unionized ammonia concentration in drinking, surface and saline waters, domestic and industrial wastes. This SOP was written using US EPA Method 350.1 and Standard Methods 4500-NH_3B-97 and 4500-NH_3G-2011 as distillation and analysis references for total ammonia; and the Illinois Rules and Regulations, Title 35: Subtitle C, as a reference for the unionized ammonia and ammonium ion calculation.

On occasion, clients request slight modifications to this SOP. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP) and authorized via laboratory signature approval; and amended to the data packages case narrative.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants" with additional details are provided in the Eurofins Corporate SOP, *NDSC-US-TS-SOP42091,* Detection and Quantitation Limits and the Eurofins Chicago SOP, *UP-QA-017, Method Detection Limit Studies.* MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; the MDL Studies are performed and verified on an annual basis, verifying the Lower Limit of Quantitation (LLOQ) for the method.

1.1.2 Demonstration of Capability

Before the laboratory may institute a new method and begin reporting results, the laboratory shall confirm that it can properly operate the method. A demonstration of capability is performed whenever there is a change in instrument type, method or personnel. An Initial Demonstration of Capability (IDOC) must be thoroughly documented and approved by the Department Manager/Supervisor and QA Manager prior to independently analyzing client samples. All associated documentation must be retained in the QA Department and in the Analyst Training files. For additional details on the demonstration of capability procedures followed, refer to the laboratory SOP, *UP-QA-QAM, Quality Assurance Manual, Sections 19.4.2 and 19.4.3.*

1.1.3 Reporting Limits (LLOQ)

Reporting Limits (LLOQ) are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. The laboratory maintains reporting limits that are higher than the MDL. Wherever possible, reporting is limited to values approximately 3-5x the respective MDL to ensure confidence in the value reported.

Matrix	Reporting Limit
Waters	0.20 mg/L as N
Soils / Waste	20 mg/kg as N
Unionized NH3	0.00066 mg/L as N
Ammonium Ion $NH4^+$	0.256 mg/L as N

1.1.4 Definitions

Refer to Section 3.0 of the Laboratory's Quality Assurance Manual (UP-QA_QAM).

2.0 Summary of Method

This method covers the determination of ammonia nitrogen exclusive of total Kjeldahl nitrogen. The sample is buffered at pH 9.3 to 9.7 with a borate buffer in order to decrease the hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a 0.040 N solution of sulfuric acid. The ammonia in the distillate is determined by phenate colorimetry, in which alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is intensified with sodium nitroprusside.

Note: Eurofins Chicago deviates from method 350.1 which designates boric acid as the collection fluid, by using 0.040 N sulfuric acid which is required by method 4500 NH_3 B.

Unionized ammonia and Ammonium Ion ($NH4^+$) are calculated using the total ammonia concentration, on-site sample pH, and on-site sample temperature.

2.1 INTERFERENCES

- Turbidity is eliminated by distillation and filtration if necessary.
- Residual chlorine can be removed by sample pretreatment with sodium thiosulfate. Place a drop of each water sample onto a piece of potassium iodide starch test paper. A dark purple color indicates the need for treatment. Add a few crystals at a time of sodium thiosulfate to the sample until the test paper shows no color when a drop of sample is applied. If any sample needs treated, QC must be treated. Note: This should be done in the field or at the latest upon receipt, as chlorine reacts with ammonia.
- Sulfide interference should be removed by acidifying the sample with HCl and aerating vigorously until no sulfide odor is detected.
- It is difficult to store samples, reagents, or water in the laboratory without getting contamination from air-borne ammonia. All containers should be kept tightly capped.
- The addition of EDTA reduces metals interferences, specifically Ca and Mg.
- pH of samples and wash water must be similar.
- True color in the 670 nm range will positively interfere.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual, Lab Specific Addendum to the CSM, and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the

assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coat and closed-toe, nonabsorbent shoes are a minimum.

3.1 Specific Safety Concerns or Requirements

- Extra precautions should be taken when handling any hazardous chemicals, such as liquefied phenol. Prepare the reagent under a hood and use it in a separate laboratory area from where phenolics analysis is done.
- When distilling samples always have heat protective gloves available.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material[1]	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Ammonia	Corrosive Poison	50 ppm-TWA	Vapors and mists cause irritation to the respiratory tract. Causes irritation and burns to the skin and eyes
Sodium Hydroxide	Corrosive	2 mg/m3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Liquefied Phenol	Corrosive Poison	5 ppm-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Sodium nitro-ferricyanide	Toxic	5 mg/m3 as HCN gas	Warning! May cause respiratory tract irritation. May cause eye and skin irritation. Toxic if swallowed, inhaled or absorbed through the skin. Contact with acids liberates hydrogen cyanide, a very toxic, flammable gas or liquid. Target Organs: Blood, central nervous system, cardiovascular system.
Sodium Hypochlorite	Corrosive	0.5 ppm-TWA	Vapors are irritating to the upper respiratory tract. Prolonged exposure may result in delayed pulmonary edema. Contact with liquid or vapor causes irritation or burning sensation. Causes irritation, sensitization. Affects eyes, skin and respiratory system.

Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
EDTA		None	Mild irritation to reparatory tract. Symptoms may include coughing and sneezing. Low toxicity by ingestion. Prolonged contact with skin may cause redness or inflammation.
Nessler's Reagent	Corrosive Poison	2mg/m3-Ceiling	Poison! Danger! May be fatal if swallowed. Harmful if inhaled or absorbed through skin. Corrosive. Burns to any area of contact. Mercury compounds affect Kidneys and CNS. May cause skin reaction.
Thymolphthalein	Flammable Toxic	200 ppm–TWA (Methanol)	Flammable liquid. Primarily toxic by ingesting. If ingested, give large quantity of water and induce vomiting. Contact may cause dryness and cracking of the skin. May cause irritation to the eyes. Wash areas of contact with water. May cause irritation of the respiratory system.
[1] – Always add acid to water to prevent violent reactions. [2] – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 EQUIPMENT AND SUPPLIES

4.1 Equipment

- rAPID-T semi-automated spectrophotometer, capable of measuring at 660 nm
- Seal AQ700 :software AQ software version 2.5.01A43
- Software – rAPID-T (Astoria Pacific Inc.) 1.3.3.5
- 2.0 mL sample cups, polystyrene, conical
- Reaction cuvettes (Seal Analytical Inc. Part No. 5000)
- Reagent wedges (Seal Analytical Inc. Part No. 5010)
- Cuvettes
- pH Meter – Calibrated per Eurofins Chicago SOP UP-WC-pH, current year revision

4.2 Glassware and Miscellaneous supplies

- Class A graduated cylinders, 25, 50 & 100 mL
- 50 mL disposable screw-cap vials
- 5 mL dispenser containing sodium borate buffer
- 10 mL dispenser containing 0.040 N sulfuric acid
- Various Eppendorf pipettes
- 4.0 mL sample cups (rAPID-T)
- Reaction cuvettes
- reagent bottles
- KI test strips
- 50 mL, 200 mL, and 500 mL class A volumetric flasks

5.0 STANDARDS AND REAGENTS

5.1 Stock Standards

5.1.1. Stock standards are purchased from an approved vendor. If no expiration date is provided, the stock standard solutions may be used for up to one year from open date and must be replaced sooner if verification from an independent source indicates a problem.

5.2 Intermediate / Working Standards

NOTE: All standards and reagents are prepared with fresh, ammonia-free Milli-Q water unless otherwise stated, in Class A volumetric flasks. Only reagent grade ACS compliant chemicals are used. Ammonia is commonly present in laboratory air at concentrations that can affect reagents, standards and the samples themselves. Keep all containers tightly capped and away from areas of the lab where such chemicals as ammonium acetate or ammonium hydroxide are used, such as the Cr+6 by IC laboratory areas.

5.2.1. Intermediate / Working standards are prepared as dilutions from the stock standards. Intermediate / working standard solutions shelf life and are stored according to table below.. The intermediate / working standard solution must be replaced if verification from an independent source indicates a problem. Formulas may be found in TALS to prepare all listed reagents.

Reagent	Shelf Life	Storage Requirements
TKN / Ammonia Stock 1	6 months	Room Temp
TKN / Ammonia Stock 2	6 months	Room Temp
0.04N Sulfuric Acid	1 year	Secondary container
Sodium Borate Buffer	1 year	Secondary container
6 N Sodium Hydroxide	1 year	Plastic container
2 M Potassium Chloride	1 year	NA
Anti-Foam	5 years or vendor's recommendation	None or vendor's recommendation
Sodium Thiosulfate	5 years or vendor's recommendation	None or vendor's recommendation
Nitroferricyanide Solution	1 month	Room temp in dark
Salicylate Solution	1 month	4°C ± 2°C in dark
Liquefied Phenol	vendor's recommendation	Secondary container at room temp
Dichloroisocyanurate (DCI)	2 days	NA
EDTA Solution	1 month	Amber secondary container at room temp
5N Sulfuric Acid	1 year	Room temp
Phenol & Nitroferricyanide Solution	3 days	NA
Calibration diluent	1 year	NA
Hypochlorite Solution	Daily	NA
Nessler's Reagent	1 year or vendor's recommendation	None or vendor's recommendation
2% H2SO4	1 year	Secondary container
1N NaOH	1 year	Plastic container
Thymolphthalein	1 year	Protect from freezing and physical damage. Store in secure, flammable storage area away from all sources of ignition.

5.3 Quality Control Preparation

Dilute as listed below using either an Eppendorf and/or volumetric pipettes. Less volume may be used as long as the ration stays the same.

QC Sample	Stock Sol. 1 (µL)	Stock Sol. 2 (µL)	Final Volume (mL)
Method Blank (MB) Initial/Continuing Calibration Blank (ICB/CCB)			100
Initial Calibration Verification (ICV) / Lab Control Sample [1] (LCS) (2.0 mg-N/L)		100 µL	50
Continuing Calibration Verification (CCV) (4.0 mg-N/L)	200 µL		50
Matrix Spike (MS) [2] - Waters (2.0 mg-N/L)		50 µL	25
Matrix Spike (MS) [2] – Soils (2 mg-N/L in 100 mL distillate)		50 µL	0.25g soil in 25 ml KCL
RL level standard for MDL Study (0.20 mg/L) also the MRL[3]		20 µL	100

[1] LCS Duplicate (LCSD) is performed only when insufficient sample is available for the MS/MSD or when requested by the client/project/contract.
[2] Matrix Duplicate (DU) is performed only when requested by the client/project/contract. The MS and MSD are the routinely performed matrix QC indicators. The sample selection for matrix QC, if not pre-designated by the client, is rotated among client samples so that various matrix problems may be noted and/or addressed.
[3] The MRL verification check standard is required to be analyzed on a daily basis when South Carolina samples are to be analyzed by SM4500NH3 G-2011.

6.0 CALIBRATION

6.1 Manual preparation Curve

Use an Eppendorf and/or volumetric pipette to dilute to a final volume of 50 mL with calibration diluent (AQ700) or Mill-Q water (rAIPD-T)

Standard	AQ700 Volume of Stock 1 (µL)	rAIPD-T Volume of Stock 1 (µL)
0 mg/L	0	0
0.1 mg/L	NA	5
0.2 mg/L	10	10
0.5 mg/L	25	25
1.0 mg/L	50	50
2.5 mg/L	125	NA
3.0 mg/L	NA	150
5.0 mg/L	250	250
7.5 mg/L	375	NA
10.0 mg/L	500	NA

6.2 Automated preparation Curve

The curve is prepared by the instrument from a 10.0 mg/L NH3-N standard.

7.0 PROCEDURE

7.1 Quality Control Checks

Quality Controls	Frequency	Control Limit
MB	1 in20 samples	< Reporting Limit (< ½ RL per QAPP)
LCS	1 in 20 samples	86 - 113 % (Statistical); 90 –110% (SC Samples) 90-110 % (350.1)
MS	1 in 20 samples 1 in 10 samples (350.1)	75 – 125% 90-110% (350.1)
MS Duplicate (MSD)	1 in 20 samples 1 in 10 samples (350.1)	≤ 20 RPD ≤ 10 RPD (350.1)

- Statistical control limits are available for those clients or projects that require the use of statistical limits.
- Client-specific QAPPs may include QC limits and frequency requirements that supersede those given above.

7.2 Sample Preservation and Storage

Sample containers, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client request. Listed below are the holding time and the reference which includes container and preservation requirements for compliance with the Clean Water Act (CWA).

Regulation	Holding Time	Reference	Sample Preservation and Storage
CWA (NPDES)	28 days	40 CFR Part 136.3	Cool to ≤ 6 °C; H_2SO_4 to pH < 2

7.3 Sample Preparation

7.3.1 Sample Size

Matrix	Sample Size
Waters	25 mL
Soils / Wastes	~0.25 gram to 25 mL with 2 M KCl
[1]Sludges / Oils	~0.25 gram to 25 mL with 2 M KCl

[1]More sample may be used for sludges high in water content when a low dry weight reporting limit is required.

Wastes, sludges and oils are distilled in a 2 M KCl salt solution instead of Milli-Q water. This procedure uses, as a guideline, Method 1 for ammonia analysis in sediment found in "Procedure for Handling and Chemical Analysis of Sediment and Water Samples" (Technical Report, EPA/CE-81-1).

7.3.2 Pre-Distillation Step

If a sample's distillate is known to precipitate upon the addition of color reagent, the sample may be pre-distilled by the following protocol to remove interferences. An LCS and an MS/MSD must be pre-distilled with the sample to demonstrate no loss of ammonia. Care must be taken to link the pre-distilled LCS with only the affected sample(s). Document the pre-distillation on the raw data.

7.3.2.1 Pour a small amount of sample into a disposable beaker and test with pH paper to ensure that the pH is <2.

7.3.2.2 Dispense 100 mL of sample into a distillation flask and add 30 mL of Milli-Q water. Distill 30 mL of distillate.

7.3.2.3 Dispose of the 30 mL of distillate and proceed to Section 7.3.4.

7.3.3 Distillation

7.3.3.1 Turn on the hot block to allow it reach temperature set point.

7.3.3.2 Prior to distillation of sample, pour a small amount of sample into a disposable beaker. Add a drop of each sample to a moistened KI test strip to check for chlorine and treat if necessary. (Section 2)

7.3.3.3 Add 1.25 mL of Sodium Borate to 25 mL of sample contained in the distillation flask.

7.3.3.4 Check the pH and adjust to 9.3 to 9.7 with 6 N Sodium Hydroxide using a calibrated pH meter.

7.3.3.5 Add 1-2 boiling chips. Also add anti-foam if sample is cloudy or has solids.

7.3.3.6 Cap each tube, making sure an O-ring is present, then insert a reagent addition straw though the cap and into each sample tube.

7.3.3.6 Add 10 mL of 0.04N sulfuric acid to each collection trap and attach it to the vacuum manifold.

7.3.3.7 Place the rack of tubes containing the samples into the hot block and quickly attach the collection traps.

Note: It is important to be aware that most of the ammonia is released quickly, so ensure that the traps are connected to the tubes rapidly.

7.3.3.8 Distill for 1 hour. Transfer the distillate from the collection trap to a 25 mL graduated cylinder and dilute to 25 mL with Milli-Q Water. Store the distillate in the tightly closed screw-cap vial until the colorimetric determination.

7.3.4 Optional Spot Test for dilution determination

Pour a few mL of distillate into a 10 mL test tube and add a few drops of Nessler's Reagent. Based on the color development, a dilution can be estimated for the colorimetric analysis. You may wish to compare the color intensity visually to that of a tube of the high standard of the curve treated the same way. Make sure to record that a spot test was done in ADII. Alternatively, color the distillates

per section 7.6.1 and make dilutions as necessary. Be sure to read all undiluted preparations as well as the in-range dilutions.

7.4 Calibration / Standardization

Initial Calibration procedures (calibration curve) establish the calibration range of the instrument and determine the instrument response over that range. The Continuing Calibration Verification is used within the analytical sequence to verify stable calibration throughout the sequence, and/or to demonstrate that the instruments response did not drift during a period of non-use of the instrument. Refer to the Eurofins Corporate Policy, NDSC-QA-QP44940, *Calibration Curves and the Selection of Calibration Points* and the *Calibration Criteria Training, Inorganics* Document CHI-22-09-472 for further guidance.

7.4.1 Calibration Standards

Calibration Controls	Sequence / Frequency	Control Limit
Calibration Curve (Linear – 1st Order)	Daily - prior to samples	x-intercept < Reporting Limit; Corr. Coeff. r ≥ 0.995
ICV	after the standards	90 – 110 %
ICB	after ICV	< Reporting Limit < ½ RL (per QAPP)
CCV	every 10 readings or at the end of the run	90 – 110 %
MRL	Daily with SC samples by SM4500NH3_G-2011	70 – 130%
CCB	after every CCV	< Reporting Limit < ½ RL (per QAPP)

7.5 Preventive Maintenance

Perform all the pre-analytical and post-analytical daily and less frequent steps as outlined in the Systea Easy Chem Maintenance Summary in the Systea instrument maintenance log book or follow the maintenance schedule on the AQ 700 (Attachment 2)

7.6 Sample Analysis

7.6.1 AQ700

See Attachment 1 for instructions.

7.6.2 rAIPD-T

7.6.2.1 Turn on the rAPID-T and allow it to warm up for 30 minutes prior to use. Run the start of day program.

7.6.2.2 Make sure there are no air bubbles in the syringe. If bubbles are present, use ethanol or propanol to dislodge them. Substitute a beaker of alcohol for the rinse water and prime the syringe 5 or more times. If this doesn't work, remove the syringe and manually flush with alcohol to remove all air bubbles. Prime the syringe 5 or more times with water to remove the alcohol from the system.

7.6.2.3 The instrument will automatically select the most recently used method. Be sure to verify that the correct method is selected: Ammonia, Phenate (T023).

7.6.2.4 Fill all reagents to the neck of the bottle and place in the appropriate location of the instrument. Be sure to make sure there are new cuvettes in the rack and clear the cuvette rack in the software.

7.6.2.5 Pour sufficient sample into cups and place in the instrument. A single CCV and CCB cup may be filled and used throughout the run. Analyze a CCV/CCB pair at the start of each day, after every ten samples, and at the end of the run. An initial CCV/CCB pair is not needed if samples are analyzed immediately following an initial calibration.

7.6.2.6 Scan samples and QC to the instrument queue and start the instrument.

7.6.2.7 At the end of the run the calibration and results are printed. Results are also exported to TALS. From the File menu select Export, then Data File. Click the folder icon by the destination and select the SM4500NH3_G(350.1) folder.

7.7 Documentation

7.7.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

7.7.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

7.7.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs are scanned and attached to the Documents section in the LIMS analytical batch.

7.7.4. Record all sample results and associated QC directly into LIMS. Level I and Level II reviews are performed in LIMS.

Examples of items included in the above reviews are as follows:

- QC data are outside the specified control limits for accuracy and precision
- Unusual detection limit changes are observed
- Samples having unusually high results
- Samples exceeding a known regulatory limit
- Raw data indicating some type of contamination or poor technique
- Inconsistent peak integration (if applicable)
- Transcription errors
- Results outside of calibration range

8.0 QUALITY CONTROL

8.1 QC Summary

8.1.1 At least one MB and LCS will be included in each laboratory lot of 10 or 20 samples (see section 7.0). The MB will be examined to determine if contamination is being introduced in the laboratory. The MB and LCS must be carried through all stages of the sample preparation and measurement steps.

8.1.2 Accuracy will be measured by the percent recovery (%R) of the LCS. The recovery must be within control limits (Section 7.1) in order to be considered acceptable.

8.1.3 Precision will be measured by the reproducibility of the MSs and will be calculated as Relative Percent Difference (RPD). If MSDs were not analyzed, precision will be measured using the LCS/LCSD. The recoveries must be within control limits in order to be considered acceptable.

8.1.4 One MS/MSD is performed per matrix per 10 or 20 sample analytical set (unless otherwise required by the method or a specific QAPP).

8.2 Corrective Actions

When an out of control situation occurs, the analyst must use his/her best analytical judgment and available resources to determine the corrective action to be taken. The out of control situation may be caused by more than one variable. The analyst should seek the assistance of his/her immediate supervisor, QA personnel, or other experienced staff if he/she is uncertain of the cause of the out of control situation. The test must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out of control situation should be reanalyzed. Out of control data must never be released without approval of the section supervisor, the inorganics manager, QA personnel, project manager or the laboratory director.

Listed below are steps that MUST be taken when an out of control situation occurs:

- demonstrate that all the problems creating the out-of-control situation were addressed;
- document the problem and the action which was taken to correct the problem on the data review checklist;
- document on the data review checklist that an in-control situation has been achieved; and
- receive approval (signature) of the section supervisor, inorganics manager, QA personnel, project manager, or laboratory director prior to the release of any analytical data associated with the problem.

Suggested Actions to specific out-of-control situations follow. Frequently, there are client-specific QAP requirements for corrective actions that may supersede the following actions.

8.2.1 Calibration Curve

- reanalyze the standard curve;
- prepare new stock and/or working standards;
- check reagents/solutions and prepare fresh if necessary.

8.2.2 Initial Calibration Verification (ICV)

- reanalyze the ICV to verify proper preparation;
- prepare new ICV from original stock;
- check for instrument base-line drift;
- re-standardize with existing standards, reanalyze;
- check reagents/solutions and prepare fresh if necessary; and
- prepare new stock and/or working standards and recalibrate.
- If for holding time or any other reason data are reported bracketed by a too high or low ICV, an NCM must be written.

8.2.3 Initial Calibration Blank (ICB)

- prepare a new ICB to verify proper preparation;
- verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability;
- determine the source of contamination by the process of elimination, correct the problem and reanalyze. (Carry over from a previous analysis or reagent contaminations are two common sources).
- If for holding time or any other reason data are reported bracketed by a too high or low ICB, an NCM must be written.
- Often, non-detects can be reported when bracketed by a high ICB, since those samples are not affected by a high bias.

8.2.4 Laboratory Control Sample (LCS)

- re-read the LCS to verify that an out-of-control situation exists; this refers only to the final reading, and if the re-reading is within limits, all the remaining QC and sample preparations must be re-read as well;
- if the re-reading of the LCS confirms the contamination or low recovery, determine the source of error, correct the problem and repeat the sample set. (Sources of error include but are not limited to the preparation or mixing of the standard solution, faulty distillation technique, or ammonia contamination in Milli-Q or distillation apparatus); and;
- if the recovery of the LCS is high, all non-detected sample results may generally be reported. Note out-of-control LCSs in an NCM.

8.2.5 Method Blank (MB)

- reanalyze the MB to verify contamination at a level > Reporting Limit; this refers only to the final weighing or colorimetric step of the analytical process, and if the re-analysis is less than the Reporting Limit, all the remaining QC and sample preparations must be re-read as well;
- if the re-reading of the blank confirms the contamination, determine the source and correct the problem; and
- all samples whose concentration is <10 times the MB level must be reprocessed and reanalyzed; any sample which is >10 times the MB level need not be reanalyzed.
- Note out-of-control MBs in an NCM.

8.2.6 Matrix Spike (MS) / MS Duplicate (MSD)

- the spiked sample must be reprocessed and reanalyzed unless the sample concentration exceeds the spike concentration by a factor of 4 times;
- if a single spike is performed and it is outside the acceptance limits, it must be repeated to verify the matrix effect. Generally, an MS and MSD are performed together in the same batch as the original sample analysis, but may be done in separate batched if necessary and related manually in LIMS.
- report all spikes, whether or not they are in control.
- Note out-of-control spikes in an NCM.

8.2.7 Matrix Duplicate (DU) - If Required

- the sample must be reprocessed and reanalyzed unless the sample concentration is <5 times the Reporting Limit, then the ± Reporting Limit rule applies;

- if the reanalysis is within the control limits, the second duplicate value is reported; a corrective action report must be written and approved by your section manager; and
- if the reanalysis is still outside of the control limits, the closer two results are generally reported
- Note out-of-control DUs in an NCM.

8.2.8 Continuing Calibration Verification (CCV)

- repeat CCV to verify proper preparation;
- prepare new CCV from original stock;
- check for instrument base-line drift;
- check reagents/solutions and prepare fresh if necessary;
- recalibrate with a new standard curve and repeat all samples since the previous in control CCV;
- never dispose of any samples until you are sure that all QC are within their designated control limits
- If for holding time or any other reason data are reported bracketed by a too high or low CCV, an NCM must be written.

8.2.9 Continuing Calibration Blank (CCB)

- prepare a new CCB to verify proper preparation;
- verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability;
- determine the source of contamination by the process of elimination, correct the problem and reanalyze all the samples since the previous in control CCB. (Carry over from a previous analysis or reagent contaminations are two common sources);
- never dispose of any samples until you are sure that all QC are within their designated control limits.
- If for holding time or any other reason data are reported bracketed by a too high or low CCB, an NCM must be written.

8.2.10 Method Reporting Limit Check Standard (MRL): Note: This is a Required Daily Check with SC Samples

- repeat MRL to verify proper preparation;
- prepare new MRL from original stock;
- check for instrument base-line drift;
- check reagents/solutions and prepare fresh if necessary;
- recalibrate with a new standard curve and repeat all samples since the previous in control MRL;
- never dispose of any samples until you are sure that all QC are within their designated control limits
- If for holding time or any other reason data are reported bracketed by a too high or low MRL, an NCM must be written.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 Waters

$$mg - \frac{N}{L} = \frac{Sample\ Conc\ From\ Curve\ (mg/L) \times Dilution\ \times Fina\ \ Dist\ Volume\ (mL)}{Sample\ Volume(mL)}$$

9.2 Wastes

$$mg - \frac{N}{Kg} = \frac{Sample\ Conc\ From\ Curve\ (mg/L) \times Dilution\ \times Final\ Dist\ Volume\ (mL)}{Sample\ Volume(g)}$$

NOTE: This is a wet weight calculation. All dry weight corrections are made in TALs at the time the analytical batch is processed.

9.3 Un-Ionized Ammonia Concentration

The following calculation is performed in TALs in the Unionized Ammonia batch:

$$Unionized\ Ammonia\ (mg/L) = \left(\frac{17}{14}\right) \times \left(\frac{Ammonia\ (mg/L)}{10^{(pKa-\ \ )} + 1}\right)$$

$$pka = 0.09018 + \frac{2729.92}{Temp\ (℃) + 273.2}$$

Temp and pH in the above formulas are the field measurements which are recorded in the field sampling records. If data is not provided on the chain of custody, contact the project manager.

9.4 Ammonium Ion Concentration

The following calculation is performed in TALs in the Unionized Ammonia batch:

$$Ammonium\ ion\ (mg/L) = \left(\frac{18}{14}\right) \times\ Unionized\ Ammonia\ (mg/\ \ ) \times 10^{(pKa-p\ \ )}$$

The pKa and pH values are the same as the unionized ammonia equation.

9.5 Accuracy

9.5.1 ICV/CCV, LCS % Recoveries

$$\frac{Observed\ Concentration}{Actual\ Concentration} \times 100$$

9.5.2 Matrix Spike % Recovery

$$\frac{Spiked\ Sample\ Conc. - Origina\ \ Sample\ Conc.}{Spike\ Concentration} \times 100$$

9.6 Precision

9.6.1 Relative Percent Difference (RPD)

$$RPD = \frac{|Original\ Sample\ Value - Duplicate\ Sample\ Value|}{\frac{[(Original\ Sample\ Value + Duplica \quad Sample\ Value)]}{2}} \times 100$$

10.0 Pollution Control

It is Eurofins policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

10.1 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to UP-WM-001.

The following waste streams are produced when this method is carried out.

- Waste containing sodium nitroferricyanide may not be disposed of in sewer drain.
- The liquid waste from pre-testing with Nessler's reagent contains mercury and must be placed in the drum labeled "Heavy Metal Corrosive Waste Water".
- Waste containing Thymolphthalein reagent will be collected in the Heavy Metals wastewater drum using a funnel to reduce splashing.
- Remaining waste will be collected in approved containers and poured into the carboy labeled Corrosive Waste Water.

11.0 Method Performance Criteria

Refer to Sections 1, 6, 7 and 8.

12.0 References

Refer to Section 1.

13.0 Attachments

Attachment 1: Sample Analysis on AQ700
Attachment 2: Example of AQ700 maintenance
Attachment 3: AQ Baseline

14.0 REVISION HISTORY

- Revision 14 updated on 04/15/24
- External Audit
- Section 1.10 updated corporate SOP
- Section 2.0 updated deviation from method 350.1 and note to treat QC if samples are
- Throughout added reference to AQ700 instrument.
- Section 5.0 updated reagents, added formulas in TALS and added table for reagent shelf life and storage requirements.
- Section 5.18 moved to Section 6.1 and 6.2
- Section 7.1 combined charts
- Section 7.6 Added reference to attachment 1 for AQ700 sample analysis
- Rewrote Section 7.7
- Added AQ 700maintenance attachments

Attachment 1.

Sample Analysis on AQ700 (CHI-22-12-189/A-3/24)

Sample Analysis on AQ700

Perform "Daily Startup" in the maintenance and setup tab
Fill reagent wedge(s) with reagent(s) as listed in Table 1 and place the wedge(s) into the reagent tray.

TABLE 1

Method	Reagent Wedge #	Reagent
TKN	5	TKN Working buffer
	6	Working Salicylate nitrofericyanide
	7	Sodium hypochlorite
	22	TKN synthetic blank matrix
Nitrite	16	Sulfanilamide-nedd
Phosphorus	3	Working color reagent
	4	Working ascorbic acid
Phenol	13	4-Aminoantipyrine (AAP)
	14	Potassium Ferricyanide
Nitrate-Nitrite	2	NOx Diluent
	16	Sulfanilamide-nedd
Ammonia	3	Salicylate
	4	DCI
	21	Calibration diluent

Double-click "scheduling" in the AQ700 software, and select a tray number and reagent set. Name the tray with today's date, [test name], and a letter to designate the run number. See Table 2 for information.

TABLE 2

Method	Reagent Set	Test Name
TKN	1	TKN022824A
Nitrite (N02)	1	031524N02A
Phenol	1	Phenol022924A
Phosphorus	2	ophos022824a Tphos022824a
Nitrate (N03)	1	031524N03A
Ammonia	1	022824NH3A

Starting with cup 1, add the QC into the schedule. (ICV, ICB, MB, LCS) Then, scan in the samples, including MS/MSD.

NOTE: there is no need to add any CCVs/CCBs to the schedule. The software automatically inserts them every 10 samples.

Highlight all of the QC and samples in the schedule and select the correct test from available tests (See Table 3). To add any dilutions, highlight the desired sample(s), select the dilution factor, and click [test] for a second time. This will add an auto-dilution to any highlighted samples.

TABLE 3

Method	Test Name
TKN	TKN
Nitrite	N02
Phenol	Phenol
Phosphorus	oP
Nitrate	Nitrate
Ammonia	NH3

Remove one of the four trays from the instrument, and using 2mL sample cups. Load the tray according to the schedule generated above.

NOTE: See Table 4 for respective cups that he CCV and High calibration standard should be placed in.

TABLE 4

Method	Cup Positions	
TKN	103	104
Nitrite	88	89
Phenol	105	106
Phosphorus	105	106
Nitrate	105	106
Ammonia	105	106

On the “run” screen, select “tray placement.” Select the tray that corresponds to the tray loaded above. Select the schedule associated with the tray as well as reagent set (Table 5). Select “okay.”

TABLE 5

Method	Reagent Set
TKN	1
Nitrite (N02)	1
Phenol	1
Phosphorus	2
Nitrate (N03)	1
Ammonia	1

On the “run” screen, select auto start. On the pop-up that follows, check any necessary boxes (perform calibration, replace cuvettes, etc.) and select “okay” The next pop up will only appear if an auto-calibration was requested. Ensure the correct method is checked, and click “okay.”

When the run is complete, double click “data review,” and select the desired tray. If dilutions are required, add the necessary dilution factor by selecting “dilution factor” and press “okay.” Highlight the desired sample, and select “auto dilution.” This will add the dilution factor, as well as reschedule the sample. Be sure to reschedule necessary CCVs and CCBs by highlighting them and selecting “reschedule.”
Once analysis is truly complete, select the tray in the “data review” tab and click “accept all.” The software will ask if the user is sure. Click “yes” and the software will generate a CSV file with the results. Name the file and save it into the “out” folder. Copy the CSV file, and paste it into the test (Table 6) Tals transfer folder.

TABLE 6

Method	TALS Transfer Folder	Import Path
TKN	TKN	\\corptalsapp16\500-CH-RawData\WetChem\Seal3\SM4500_TKN_H(TKN_DIL)
Nitrite	N02	\\corptalsapp16\500-CH-RawData\WetChem\Seal3\SM4500_NO2_B(NO2)
Phenol	Phenol	\\corptalsapp16\500-CH-RawData\WetChem\Seal3\420.4(PhenolTR)
Phosphorus	Phosphorus	\\corptalsapp16\500-CH-RawData\WetChem\Seal3\4500_P_E(TPHOS) \\corptalsapp16\500-CH-RawData\WetChem\Seal3\4500_P_E_Ortho(Ortho1)
Nitrate	Nitrate	\\corptalsapp16\500-CH-RawData\WetChem\Seal3\4500NO3F(NO3_NO2)
Ammonia	Ammonia	\\corptalsapp16\500-CH-RawData\WetChem\Seal3\SM4500NH3_G(350.1)

Under “reporting” in the AQ software, select the tray, and generate the “Eurofins 1.0” report. On the right side of the page, the software will present a preview of the document. Right click on the document and select “print.” Print the report to a PDF and save it into the [test] folder (wetchem – raw data for printing –[test]) with the date of analysis, [test], and the letter designating the run number (Table 7).

TABLE 7

Method	Test Folder	EX: Name
TKN	TKN	TKN022824A
Nitrite	N02	031524N02A
Phenol	Phenol	Phenol022924A
Phosphorus	Phosphorus	ophos022824a Tphos022824a
Nitrate	Nitrate	031524N03A
Ammonia	Ammonia	022824NH3A

Attachment 2.

Example: AQ700 Maintenance

SEAL Analytical

AQ700 Daily (Morning) Tasks

	Daily (Morning) Tasks	
☑	Empty and Refill Wash Water Reservoir	
☑	Empty the Waste Container	
☑	Replace Reaction Segments as Required	
Maintenance Menu		
	☑	Observe movements during initialization • Movements should be smooth and they should be the same each initialization
	☑	**DILUTER:** Prime both Syringes (5-10 times) • Verify no air remains in syringes and they are operating smoothly.
	☑	**DILUTER:** Check operation of the Probe Wash assemblies • Turn on Waste Pumps and Wash Valve • Verify water movement through both chambers
	☑	**CUVETTE FUNCTIONS:** Perform 1-5 Auto Washes • Observe Wash Bath is Filling and Clean
	☑	**SPECTRO**: Perform 1 Auto Wash. Run Water Baselines. • Auto-gain baselines should have gain results within ± 2 from day to day operations.
☑	Inspect reagents for particulates or excessive color. Filter or replace reagents as needed. Check the method documents for information on reagent stability and symptoms of reagent degradation.	
☑	Cadmium Coil checks as required. See Cadmium Coil Care section of the Nitrate + Nitrite method documentation	

Attachment 2.

Cont'd

SEAL Analytical

AQ700 Daily (Evening) Tasks

	Daily (Evening) Tasks
☑	Place Cuvette Cleaning Solution in Reagent Position 1. Maintenance and Setup – Extra Wash
☑	Zero Segments –Maintenance and Setup, Zero Segments and discard the used reaction segments
☑	Discard used Sample Cups
☑	Empty the Waste Container
☑	Empty the Wash Water Reservoir
☑	Put Reagent Tray into the refrigerator for overnight storage
☑	If any spills on the reagents tray, clean the tray by removing the reagent wedges, wiping up spills and condensate in the tray and wiping the bottom of the wedges.
☑	If any spills on the carousel, clean the reaction carousel by removing reaction segments and wiping spills in and around the carousel
☑	Archive completed runs in Data review

Attachment 2.

Cont'd

SEAL Analytical

AQ700 Weekly Maintenance

	Weekly Tasks
☑	Record and compare water baseline voltages to monitor lamp stability. If gains change suddenly (within 2 weeks) by more than 5, the lamp may need to be replaced.
☑	Clean Sampler Wash Bath
☑	Clean Aspiration Wash Bath
☑	Clean Cadmium Reduction Well
☑	Inspect Sampler Probe – Straight, Clean, Not Dripping
☑	Inspect Aspiration Probe – Straight, Clean, Not Dripping

Attachment 3.

Example: AQ Baseline

AQ700 Water Baselines

SEAL Analytical

Software version:	2.5.01A43
User name:	Kaitlin
Time and Date:	2024-03-14 07:22:29

Filter Number	Filter	Previous water baselines	Current Water baselines
1	405	4.7341 v (Gain = 229)	4.7388 v (Gain = 229)
2	450	4.7207 v (Gain = 192)	4.7259 v (Gain = 192)
3	480	4.6852 v (Gain = 151)	4.6919 v (Gain = 151)
4	505	4.6893 v (Gain = 190)	4.6958 v (Gain = 190)
5	520	4.6865 v (Gain = 174)	4.6948 v (Gain = 174)
6	546	4.7177 v (Gain = 202)	4.7250 v (Gain = 202)
7	578	4.6708 v (Gain = 180)	4.6793 v (Gain = 180)
8	660	4.7022 v (Gain = 189)	4.7127 v (Gain = 189)
9	880	4.7551 v (Gain = 209)	4.7631 v (Gain = 209)
10	Dark	0.0273 v	0.0273 v
Time & Date		**2024-03-13 10:39:13**	**2024-03-14 07:20:13**

Eurofins Chicago
STANDARD OPERATING PRACTICE (SOP) CHANGE FORM

Original SOP Number/Revision #: UP-WC-Phosphorus Rev. 30 Last Mod ID (circle): NA/ _____

SOP Title: Phosphorus and Ortho-Phosphorus

Affected SOP Section Number(s):
Effective Date of Change:

CONTROLLED DISTRIBUTION

COPY # :
ISSUED TO : Uncontrolled

Full Signature Approvals Are Kept on File with Eurofins Chicago Standard Practice Records

Revision Number with Mod ID:

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. **Append this form to the front of the SOP copy.**

1. Reason for SOP Change:
External Audit

2. Summary of Procedure Change (circle to indicate if there are attachments t this form: No / Yes: # pages attached = ___)
Section 1.1.1 and section 1.1.2 MDLs must be verified every 6 months.

Initiated/Reviewed By: Name/Date — 7/15/24

NA
Initiated/Reviewed By: Name/Date

Approval Signature/Date: Section Manager — 7/15/24

Approval Signature/Date: QA Manager or Designee — 7/15/24

TITLE: WET CHEMISTRY
Phosphorus and Ortho-Phosphorus

Approvals (Signature/Date):

Paul Kolarczyk 3-20-24
Paul Kolarczyk Date
Supervisor, Wet Chemistry

Chris Hoham 3/20/24
Chris Hoham Date
Env. Health & Safety Coor.

Nicole Berg 3/20/24
Nicole Berg Date
Quality Assurance Manager

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1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) outlines the guidelines for the determination of Phosphorus and Ortho-Phosphorus in water and waste matrices, including soils and sediments. This SOP was written using Standard Methods 4500-P B-99 for preparation and EPA 365.1, SM4500-P E-99, SM4500-P E-2011, and SM4500-P E-23rd ED for analysis as the primary references. Standard Methods 4020A and B were used as additional references concerning QC requirements for this method.

On occasion, clients request slight modifications to this SOP for non-drinking water samples. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP), authorized via laboratory signature approval, and mentioned in the data package's case narrative. **Note: There are no method modifications allowed for Drinking Water samples without prior written approval from the US EPA.**

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL), referred to as the detection limit (DL) in NELAC documents, is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136 "Guidelines Establishing Test Procedures for the Analysis of Pollutants" with additional details are provided in the Eurofins Corporate SOP, *NDSC-QA-SOP42091, Detection and Quantitation Limits* and the Eurofins Chicago SOP, *UP-QA-017, Method Detection Limit Studies.* MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; the MDL will be performed and verified on an annual basis verifying the Lower Limit of Quantitation (LLOQ) for the method.

1.1.2 Demonstration of Capability

Before the laboratory may institute a new method and begin reporting results, the laboratory shall confirm that it can properly operate the method. A demonstration of capability is performed when there is a change in instrument type, method or personnel. An Initial Demonstration of Capability (IDOC) must be thoroughly documented and approved by the Department Manager/Supervisor and QA Manager prior to independently analyzing client samples. All associated documentation must be retained in the QA Department and in the Analyst Training files. For additional details on the demonstration of capability procedures followed, refer to the laboratory SOP, *UP-QA-QAM, Quality Assurance Manual, Sections 19.4.2 and 19.4.3.*

1.1.2 Reporting Limits (LLOQ)

Reporting Limits (LLOQ) are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. The laboratory maintains reporting limits that are higher than the MDL. Wherever possible, reporting is limited to values approximately 3-5x the respective MDL to ensure confidence in the value reported.

Matrix	Description	Reporting Limit
Waters	Phosphate, Ortho as PO4	0.15 mg/L
	Phosphorous, Total as PO4	
	Phosphorous, Organic as P	0.05 mg/L
	Phosphorous, Total as P	
	Phosphate, Ortho as P	
Soils	Phosphate, Ortho as PO4	15 mg/kg
	Phosphorous, Total as PO4	
	Phosphorous, Organic as P	5 mg/kg
	Phosphorous, Total as P	
	Phosphate, Ortho as P	

Reporting limits will vary depending on sample volume/size, dilution factors, dry weight reporting (soils/waste) and annual MDL determinations. Soil reporting limits are based on 1.0 g/100 mL digestion volume.

1.1.3 Definitions

Refer to Section 3.0 of the Laboratory's Quality Assurance Manual (UP-QA-QAM).

1.2 Summary of Method

This method covers the determination of specified forms of phosphorus in surface and saline waters, domestic and industrial wastes, and soils.

Phosphorus occurs in natural waters and waste waters almost solely as phosphates. Phosphates are widely used in municipal and private water treatment systems and are commonly grouped into three types: orthophosphate, condensed phosphate and organically-bound phosphate. The results of these tests are expressed as mg P/L. If phosphate-phosphorus (mg PO_4/L) is desired, a factor of 3.066 is applied (see Section 9). If phosphorus pentoxide is required (P_2O_5), a factor of 2.291 is applied to the total P result. These two forms are programmed into Analyst Desktop.

Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue colored complex by ascorbic acid. The color is proportional to the orthophosphate concentration.

Polyphosphates and some organic phosphorus compounds may be converted to the orthophosphate form by sulfuric acid hydrolysis. Organic phosphorus compounds may be converted to the orthophosphate by the addition of persulfate or concentrated sulfuric acid.

2.0 INTERFERENCES

- High concentrations of iron cause precipitation of and subsequent loss of phosphorus.
- Arsenate is determined similarly to phosphorus. However, at concentrations found in sea water, it does not interfere.
- The phosphorus test is highly susceptible to contamination from phosphorus-containing detergents and hand-contact, only phosphate free detergent is used in the laboratory. All glassware, graduated cylinders, funnels, etc., used for sample preparation, standard

preparation, or any phase of the analysis must be rinsed with 10% hydrochloric (HCl) acid solution followed by 3 deionized (DI) water rinses. Handle the clean glassware with care.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual, Lab Specific Addendum to the CSM, and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coat and closed-toe, nonabsorbent shoes are a minimum.

3.1 Specific Safety Concerns or Requirements

There are no specific safety concerns associated with this method, other than those listed in the following section.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method.** The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material[1]	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Ammonium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
Sodium Hydroxide	Corrosive	2 mg/m^3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.

Material[1]	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Ethanol	Flammable Poison	1900 mg/m^3 per 10 hrs.	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Prolonged exposures to high concentration may cause drowsiness, loss of appetite, and inability to concentrate. If ingested will cause headaches, gastritis, intoxication, blindness and, in acute cases, death. Causes skin irritation, cracking or flaking due to dehydration and defatting action. Can cause eye irritation. Prolonged exposure may affect the nervous system, liver, kidneys, blood, g.i. tract and reproductive system. Continued ingestion of small amounts could result in blindness.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 EQUIPMENT AND SUPPLIES

- rAPID-T semi-automated spectrophotometer, capable of measuring at 660nm;
- AQ700 instrument
- Software: AQ Software Version 2.5.01A43
- Software – rAPID-T (Astoria Pacific Inc.) 1.3.3.7
- Balance capable of weighing to the nearest 0.1 mg.
- Environmental Express 36 or 54 place 50 mL Hot Block
- Large surface hot plate
- Laboratory hoods
- wrist action shaker
- 50 mL disposable digestion tubes, Environmental Express # SC475 (check that the metals group has verified that the 50 mL mark is within 2.5% tolerance for the current Lot # and file the certificate for each new lot recording the date verified and the date in use on the certificate).
- 125, 250 mL Erlenmeyer flasks
- 1 L 500 mL, 100 mL and 50 mL volumetric flasks
- 50 mL graduated cylinder
- 10 mL disposable pipettes
- various Eppendorf® pipettes
- 100 mL disposable Snap Cap Container (volume verified per lot)
- glass or plastic funnels
- laboratory timer
- laboratory scoop that delivers 0.4 grams of Ammonium persulfate
- 0.45 µm glass fiber filter
- 2.0 mL sample cups, polystyrene, conical
- Reaction cuvettes (Seal Analytical Inc. Part No. 5000)
- Reagent wedges (Seal Analytical Inc. Part No. 5010)
- Cuvettes (For rAIPD-T)

NOTE: All re-used glassware must be acid rinsed prior to use in any step of this procedure. After washing with phosphate-free soap in hot water and rinsing first with 3 rinses of tap water then 3 rinses of deionized (DI) water in the inorganics dish room, the analyst then rinses each piece, including flasks, funnels, graduated cylinders etc., with 10% HCl solution, followed by 3 DI water rinses, prior to use.

5.0 REAGENTS AND STANDARDS

5.1 Stock Standards

5.1.1. Stock standards are purchased from an approved vendor. If no expiration date is provided, the stock standard solutions may be used for up to one year from open date and must be replaced sooner if verification from an independent source indicates a problem.

5.2 Intermediate / Working Standards

NOTE: All glassware used for the preparation of standards and QC solutions must be pre-rinsed with 10% HCl and DI water prior to use. Only reagent grade chemicals that meet ACS criteria are to be used for this method.

5.2.1. Intermediate / Working standards are prepared as dilutions from the stock standards. Intermediate / working standard solutions shelf life and are stored according to table below.. The intermediate / working standard solution must be replaced if verification from an independent source indicates a problem.

Reagent	Shelf Life	Storage Requirements
11 N Sulfuric Acid	1 year	2nd container
Ammonium Persulfate	Manufacturer's recommendation	Room Temp
Phenolphthalein Indicator	1 year	NA
Concentrated Nitric (HNO_3) and Sulfuric Acid (H_2SO_4)	Manufacturer's recommendation	2nd container
10 N Sodium Hydroxide (NaOH)	1 year	2nd container
Sodium Dodecyl Sulfate (SDS), 10% w/v	1 year	Room Temp
5 N Sulfuric Acid	6 months	Room Temp
Antimony Potassium Tartrate	1 month	Amber bottle, 4°C ± 2°C
Ammonium Molybdate	Daily	Plastic container, 4°C ± 2°C
0.1 M Ascorbic Acid	7 days	4°C ± 2°C
Working Ascorbic Acid	Daily	4°C ± 2°C
Combined Color Reagent	4 hours	NA
Working Phosphate Color Reagent	3 weeks	4°C ± 2°C
Special Cleaning Solution	2 months	Room Temp
Calibration Diluent	6 months	NA
Phosphorus Working Standard I, 100 mg/L	1 Year or stock manufacture's expiration date	4°C ± 2°C
Phosphorus Working Standard II, 50 mg/L	1 Year or stock manufacture's expiration date	4°C ± 2°C

5.2.1.1 Special Cleaning Solution

In a 100 mL volumetric flask, dissolve 4.0 g of sodium hydroxide in ~ 80 mL of DI water. Add 1.0 g of EDTA, and dilute to 100 mL with DI water.

- Life of Reagent: 2 months
- Storage Requirements: Store at room temperature

5.3. Refer to the LIMS standards and reagents module for further details on preparation of intermediate / working standard solutions.

5.2.5 Quality Control Preparation

5.2.5.1 Standard Curve Preparation

The calibration curve points are prepared by the rAPID-T instrument.

Volume of Source Standard (dilutions performed by the instrument and brought up to a final volume of 360 µL)	**Concentration (mg/L)**
0	0
3.6 µL	0.02
9.0 µL	0.05
18 µL	0.10
45 µL	0.25
90 µL	0.50
180 µL	1.00

Note: The source standard shall be prepared as 5 mL of Working Standard I diluted to 250 mL with DI water. The life of this source standard is 28 days.

Note: A diluter check will be performed on a quarterly basis to verify that the instrument is accurately performing dilutions. Acceptance limits are ± 2.5%, the verification will be recorded in the maintenance logbook.

The calibration curve points are prepared by the Seal AQ700 instrument.
Note: Eurofins Chicago deviates from method 365.1 Rev 2.0 by not digesting calibration.

Volume of Source Standard (dilutions performed by the instrument and brought up to a final volume of 200 µL)	**Concentration (mg/L)**
0	0
2 µL	0.05
8 µL	0.20
20 µL	0.50
50 µL	1.25
100 µL	2.50
200 µL	5.00

Note: The source standard shall be prepared as 2.5 mL of Working Standard I diluted to 50 mL with DI water. The life of this standard is 1 week.

5.2.5.2 Calibration Verification and Quality Control Preparation

QC Standard- rAIPD-T	Preparation
Initial & Continuing Calibration Blanks (ICB / CCB)	rAIPD-T: 50 mL DI water to a disposable 100 mL beaker. AQ700: ~2 mL DI water to a sample cup.
Initial Calibration Verification (ICV)[1]	rAIPD-T: 1 mL of Working Standard II diluted to 200 mL with DI water (0.25 mg/L). AQ 700 1 mL of Working Standard II diluted to 50 mL with DI water (1.0 mg/L).
Method Blank (MB)[2]	50 mL DI water to a 50 mL digestion tube.
Total Phosphorus Laboratory Control Sample (LCS)[2] (0.5 mg/L)	500 µL of Working Standard II diluted to 50 mL with DI water.
Ortho-phosphorus LCS (0.25 mg/L)	125 µL of Working Standard II diluted to 25 mL with DI water.
Continuing Calibration Verification[2] (CCV) (0.5 mg/L)	250 µL of Working Standard I diluted to 50 mL with DI water.
Ortho-phosphorus CCV[1]	rAIPD-T: 1 mL of Working Standard I diluted to 200 mL with DI water (0.5 mg/L) AQ700: . 1.25 mL of Working Standard I diluted to 50 mL with DI water 2.5 mg/L).
Reporting limit verification std. (MRL)[2] (0.050 mg/L)	25 µL of Working Standards 1 to 50 mL with DI water.

[1] Life of the standard is 28 days
[2] Must digest with samples in a batch

5.2.5.3 Matrix Spike (MS) / MS Duplicate (MSD)

Description	Preparation
Orthophosphorus – Water (0.25 mg/L)	rAIPD-T: 0.125 mL of Working Standard II to 25 mL sample (0.25 mg/L). AQ700: 0.5 mL of Working Standard II to 25 mL sample (1.0 mg/L)
Orthophosphorus – Soil (1.0 mg/L)	2.0 mL of Working Standard II to 100 mL DI water with ~ 1 gram of sample.
Total Phosphorus – Water (0.25 mg/L)	0.250 mL of Working Standard II to 50 mL sample.
Total Phosphorus – Soil (1.0 mg/L)	2.0 mL of Working Standard II to ~ 1 gram of sample. Add 50 mL DI water for digestion, then final volume of 100 mL after filtration.

Note: Add spike to solid samples prior to adding DI water.

6.0 CALIBRATION (NON-DAILY)

Not Applicable.

7.0 PROCEDURE

7.1 Quality Control Checks

Quality Controls	Frequency [1]	Control Limit
MB	1 in 20 samples	Absolute value < Reporting Limit[4] < MDL (Drinking Waters)
LCS [2]	1 in 20 samples	88 - 123% (Statistical) 80 - 120% (QAPP) 90 – 110% 365.1
Matrix Duplicate (DU) [3]	1 in 20 samples	≤ 20 RPD
MS [3]	1 in 20 samples	75 – 125%
MSD [3]	1 in 20 samples	≤ 20 RPD
MRL	Quarterly[5]	50-150%[5]

[1]Drinking water samples must have an MS & DU performed at a frequency of 1 in 10 samples per batch. The control limits are ± 15% recovery and ≤ 10 RPD, respectively. LCS control limits are 90 - 110%. Phosphorus is NOT a regulated drinking water analyte.
[2] LCS Duplicate (LCSD) is performed only when insufficient sample is available for the MS/MSD or when requested by the client/project/contract.
[3] The sample selection for MS/MSD, if not defined on the chain-of-custody, is rotated among client samples so that various matrix problems may be noted and/or addressed. DU is performed only when requested by the client/project/contract. The MS and MSD are the routine matrix QC indicators.
[4] ½ the RL is the Eurofins Chicago level of the Limit of Detection (LOD) as applied to the NELAC definition. Blanks may be flagged above this level, but remediation may not be required.
[5] Generally performed with PTs and during MDL studies, and per QAPPs as necessary. Acceptance limits may vary upon client request.

7.2 Sample Preservation and Storage

Holding time, preservation techniques and sample container may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client request. Listed below are the holding times and the references which include container and preservation requirements for compliance with the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA).

Regulation	Holding Time	Preservation[2]	Reference
CWA	28 days[1]	pH < 2, H_2SO_4	CFR 40 Pt. 136.3

[1]Only ***ortho-***phosphate has a ***48-hour*** holding time and the analysis is performed on ***unpreserved*** samples. All orthophosphorus samples need to be filtered within 15 minutes of collection.

Note: If a water sample is not field filtered, attach an NCM stating that the sample was filtered at the laboratory within the method holding time, but not within 15 minutes of collection. No flag is required.

[2] Samples are maintained at <6 ˚C prior to analysis and disposal.

7.3 Sample Preparation

7.3.1 Sample Size

Matrix	Sample Size
Waters	50 mL (25 mL for ortho-phosphorus.)
Soils / Wastes	1 gram / 100 mL DI Water

7.3.2 Ortho-Phosphorus Preparation

If necessary, adjust the pH of the sample with phenolphthalein indicator according to Standard Methods 4500-P E-99, Section 4a as follows: Add 1 drop of phenolphthalein indicator to 25 mL of sample. If a pink color develops, add a 5 N H_2SO_4 solution to just discharge the color.

Sample is filtered through a 0.45 µm glass fiber filter. Proceed to the Colorimetric Analysis in Section 7.6.

7.3.3 Ortho-Phosphorus Soil Preparation

Weigh 1.0 gram of sample into a 250 mL Erlenmeyer flask and add 50 mL of DI water. Shake for 10 minutes on a wrist action shaker, filter into a 100 mL Class A volumetric flask. Dilute to volume with DI water. Refer to Section 7.6 for the coloring procedure.

7.3.4 Total Phosphorus in Water - Ammonium Persulfate Digestion

1. Place 50 mL of sample, or an aliquot diluted to 50 mL with DI water, and all batch blanks, spikes, and standards into labeled, 50 mL disposable digestion tubes. Assemble the batch in a plastic rack for the hot block.

Note: The volume marks on the vials may be used quantitatively. Each lot is verified at 2 levels in the Eurofins Chicago metals group.

2. Add 1 mL of 11 N H_2SO_4 and 0.4 grams (1 scoop) of ammonium persulfate to each tube.

3. Place the sample rack(s) into the pre-heated hot block and set a timer for no more than 4 hours, the approximate time it takes for the preparations to evaporate to a final volume of about 10 mL. **DO NOT ALLOW THE SAMPLES TO GO DRY**.

4. Allow to cool and then dilute to ~30 mL with DI water.

5. Add 2-3 additional drops of phenolphthalein. Then add 10 N NaOH drop-wise until the sample is pink.

6. Add 5N H_2SO_4 drop-wise until the solution is just colorless. The pH should now be adjusted correctly.

7. Dilute to 50 mL with DI water. If sample is turbid at this point, turbidity should go away with addition of color reagent. Proceed to Section 7.6 for the coloring procedure.

8. If sample digestates are not analyzed on the same day as the distillation, refrigerated storage is required.

7.3.5 Total Phosphorus - Soil Preparation

The following method is modified from Standard Methods 4500-P B-99 and 4500-P B-2011, Section 4.

1. Weigh ~1.0 gram of sample to at least the nearest 0.01 g into a 250 mL Erlenmeyer flask and add 50 mL of DI water. Add 1 mL of concentrated H_2SO_4 and 5 mL of concentrated HNO3.

2. Digest to a volume of ~1 mL and then continue until the solution becomes colorless or straw-colored, allowing the digestates to fume.

3. Cool and add ~20 mL of DI water.

4. Filter the solution using a 0.45 µm glass fiber filter to remove particulate material or turbidity, into a 100 mL plastic snap cap container. Carefully rinse the sample container, filtering several times adding the filter washings to the flask.

5. Add 1 drop of phenolphthalein indicator and enough 10 N NaOH to produce a pink color. Add 5 N H_2SO_4 to just discharge the color.

6. Adjust the sample volume to 100 mL with DI water.

7. If sample is turbid after adjusting the pH, the turbidity should go away after addition of the acidic color reagent. Proceed to Section 7.6 for the coloring procedure.

8. If sample digestates are not analyzed on the same day as the distillation, refrigerated storage is required.

7.4 Calibration / Standardization

Before any instrument is used as a measuring device, the instrumental response to known reference materials must be determined. All sample measurements are made within the calibrated range of the instrument. Preparation of all reference materials used for calibration will be documented. The use of linear regression for the calibration curve is required by this method. Initial Calibration procedures (calibration curve) establish the calibration range of the instrument and determine the instrument response over that range. The Continuing Calibration Verification is used within the analytical sequence to verify stable calibration throughout the sequence, and/or to demonstrate that the instruments response did not drift during a period of non-use of the instrument. Refer to the Eurofins Corporate Policy for Calibration Curves and the Selection of Calibration Points (NDSC-QA-QP44940) and the *Calibration Criteria Training, Inorganics* Document CHI-22-09-472 for further guidance

Calibration Controls	Sequence / Frequency	Control Limit
Calibration Curve (Linear – 1st Order)	Daily - prior to samples	r ≥ 0.995 |y-int| < Reporting Limit (< ½ RL per QAPP) Standard Read-back +/- 10% (Low Standard +/- ½ RL)
ICV	after calibration	90 – 110%
ICB	after ICV	< Reporting Limit [1] < MDL (Drinking Water)
CCV	every 10 or fewer readings	90 – 110%
CCB	after each CCV	< Reporting Limit [1] < MDL (Drinking Water)

[1] ½ the RL is the Eurofins Chicago level of the Limit of Detection (LOD) as applied to the NELAC definition. Blanks may be flagged above this level, but remediation may not be required.

7.5 Preventive Maintenance

- Keep the exterior of the AQ700 and the spectrophotometer and surrounding area clean.
- Check/Fill Water Container
- Check Waste Container
- Check syringe for air bubbles
- System Check – Start of Day
- System Check – Start of Day
- System Check – End of Day
- The wavelength verification is done annually and referenced in the maintenance log.
- See the trouble-shooting and maintenance pages included in the rAPID-T Maintenance Log for additional information, and record all maintenance activities in that log promptly.

7.6 Analysis

Note: In this section, alternative sample volumes may be used for colorimetry, but the sample to color reagent ratio must stay the same. For example, 8 mL of color reagent into 100 mL sample, or 2 mL of color reagent into 25 mL of sample.

See Attachment 1, Sample Analysis on AQ700 for procedure.

7.6.1 Select either the Ortho-Phosphate or Phosphorus method; Run the start of day procedure which sets the instrument to 660 nm, allow the lamp and reaction plate to warm up.

7.6.2 The standard curve is prepared by the instrument as described in Section 5.2.5.1.

7.6.3 Pour 4 mL aliquot of the pH-adjusted digestate for total phosphate which includes the Samples, MB, LCS, CCV into the sample cups. For ortho-phosphate, filter the samples and pH adjusted if needed and pour into the sample cups. The non-prepped Instrument QC prepared as listed in section 5.2.3.2 are also poured into the 4 mL sample cups.

Note: Sample digestates that form a precipitate after the addition of the coloring reagents require a dilution prior to analysis.

7.6.5 In the rAPID-T Instrument Software for Phosphorus, the instrument is set to read two values: 1) The sample prior to the addition of the reagents (color blank) and 2) the sample after the addition of the reagents. The software is set to subtract the two absorbance readings. The raw data print-out will display an “Abs” column for the uncorrected absorbance and a “Cor Abs” column for the color corrected absorbance. Note, this color blank subtraction is performed for all standards, QC and samples in the batch, which is a requirement of the method.

7.6.6 The instrument program is set to start reading the samples after 10 minutes, reading the batch in the proper analytical sequence against the calibration curve, recording dilutions and start and end time directly on the instrument print-out.

Note: Any additional dilutions, which are performed by the instrument, follow the same timing requirement as the original samples.

7.7 Documentation

7.7.1 Traceability of Standards, Reagents, and Consumables

Upon receipt or preparation, each chemical salt, solvent, acid, standard, or other reagent is entered into the TALS reagent module where it is issued a unique ID. Further information entered into the module includes the manufacturer, lot # (if applicable), the date received or prepared, the expiration date, volume/weight received; concentration (if applicable); preparation details (if applicable), initials of the recording analyst, and the description of the item (i.e., Phosphorus Stock II, 50 mg/L). Once the record is created, a unique label is printed and affixed to the appropriate standard/reagent container. Non-standard reagents, such as acids and color reagent components, are recorded in the batch information screens of the prep batch and the analytical batch, either by scanning or copying the batches. The standards are entered in the Reagent tab in ADII, along with the volume added for final concentration calculation.

The lot numbers of consumables, such as the filters the hot block digestion tubes, as well as the hot block ID are also entered into the batch information screen of the prep batch.
Note: It is the responsibility of each analyst to monitor and correct the batch supply IDs as new reagents, new standards, or new consumable lot# are employed.

7.7.2 Data Review

Analytical data goes through a 200% review cycle. As results are generated, analysts review their work to ensure that the results generated meet QC requirements and relevant EPA methodologies. The analyst transfers the data into TALs in the Analyst Desktop module. Where non-compliance is observed, the analyst creates Non-Conformance Memos (NCMs) in TALs. Flags and data qualifiers can be method, project, program or QAPP specific. The analyst documents the initial review and sets the batch status in LIMs to 1st level review. The second level or peer review of the data is conducted by another individual who has been trained on the review process. This secondary review is documented in the same batch, making any necessary corrections to the data or additions to the NCMs as necessary. The batch is then set to 2nd level review. The raw data, including the instrument print-outs, and manual entries, and electronic files are retained for easy retrieval in accordance with the laboratory's record and retention policy outlined in the SOP, *UP-QA-QAM, Section 16*.

Examples of items included in the above reviews are as follows:

- QC data are outside the specified control limits for accuracy and precision
- Unusual detection limit changes are observed
- Samples having unusually high results
- Samples exceeding a known regulatory limit
- Raw data indicating some type of contamination or poor technique
- Inconsistent peak integration (if applicable)
- Transcription errors
- Results outside of calibration range
- NCMs

8.0 QUALITY CONTROL

8.1 QC Summary

One MB and one LCS will be included in each batch of samples. Regardless of the matrix being processed, the MB and LCS will be in an aqueous media. The MB will be examined to determine if

contamination is being introduced in the laboratory. The LCS will be examined to determine accuracy of the method and cumulative LCS data will provide precision data.

Accuracy will be measured by the percent recovery (%) of the LCS. The recovery must be within in-house default, method-specified, or statistical control limits, whichever is applicable, in order to be considered acceptable.

One MS/MSD or MS/DU set is done per matrix per 20-sample analytical batch, unless otherwise requested. Results must agree within the in-house precision and accuracy limits in order to be considered acceptable.

8.2 Corrective Actions

When an out-of-control situation occurs, the analysts must use his/her best analytical judgment and available resources to determine the corrective action to be taken. The out-of-control situation may be caused by more than one variable. The analyst should seek the assistance of his/her immediate supervisor, QA personnel, or other experienced staff if he/she is uncertain of the cause of the out of control situation. The test must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out-of-control situation should be reanalyzed. Out-of-control data must never be released without approval of the supervisor, Project Manager, QA personnel or the lab director.

Listed below are steps that MUST be taken when an out of control situation occurs:

- demonstrate that all the problems creating the out of control situation were addressed;
- document the problem and the action which was taken to correct the problem in a NCM;
- receive approval (signature) of the supervisor, Project Manager, QA personnel, or the Laboratory Director prior to the release of any analytical data associated with the problem.

Suggested Actions to specific out of control situations:

QC Indicator	Suggested Corrective Actions
Calibration Curve	• reanalyze the standard curve; • prepare new stock and/or working standards; • check reagents/solutions and prepare fresh if necessary.
ICV	• repeat the ICV to verify proper preparation; • prepare a new ICV from the original stock; • check for instrument base-line drift; • restandardize with existing standards, reanalyze; • check reagents/solutions and prepare fresh if necessary; • prepare new stock and/or working standards and recalibrate.
ICB	• prepare a new ICB to verify proper preparation; • verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability; • determine the source of contamination by the process of elimination, correct the problem and reanalyze. (Carry over from a previous analysis and reagent contamination are two common sources).

QC Indicator	Suggested Corrective Actions
LCS	• reanalyze the LCS to verify that an out of control situation exists; • determine the source of error within the preparation procedure, correct the problem and repeat the sample set. (Sources of contamination could be either the reagents, the LCS stock solution, or the preparation area.); • non-detect sample results may be reported when the LCS is biased high; • Note any discrepancies and write a NCM as needed.
MB	• reanalyze the MB to verify contamination at a level > Reporting Limit; • determine the source of contamination and correct the problem; • all samples whose concentration is <10x the MB level must be reprocessed and reanalyzed unless the result is less than the RL; any sample which is >10x the MB level need not be reanalyzed; • Note any discrepancies and write a NCM as needed.
DU	• the sample must be reprocessed and reanalyzed unless the sample concentration is <5x the Reporting Limit, then the ± Reporting Limit rule applies; • if the reanalysis is within the control limits, the second value is reported; • if the reanalysis is still outside of the control limits, it must be documented on the data review checklist and then approved by the supervisor; • Note any discrepancies and write a NCM as needed.
MS	• If a single spike is performed and it is outside the acceptance limits, it must be repeated to verify the matrix effect. Generally, and MS and MSD are performed together in the same batch as the original sample analysis. Report all spikes, whether or not they are in control. • Note out-of-control spikes and write a NCM as needed.
CCV	• repeat the CCV to verify proper preparation; • prepare a new CCV from the original stock; • check for instrument base-line drift; • check reagents/solutions and prepare fresh if necessary; • recalibrate with a new standard curve and repeat all samples since the previous in control CCV; • never dispose of any samples until you are sure that all QC are within their designated control limits.
CCB	• prepare a new CCB to verify proper preparation; • verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability; • determine the source of contamination by the process of elimination, correct the problem and reanalyze all the samples since the previous in control CCB. (Carry over from a previous analysis or reagent contamination are two common sources). • never dispose of any samples until you are sure that all QC are within their designated control limits.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 mg P/L = (conc. from curve)(dilution factor)

9.2 mg P/kg (wet wt.)

$$\frac{(\text{conc. from curve}) \times (\text{final volume (mL)}) \times (\text{dil factor})}{\text{sample size (g)}}$$

NOTE: All dry weight corrections are made in LIMS at the time the data are entered. The final result will not calculate unless the % solids is available and at second level review.

9.3 Phosphorus conversions (mg PO_4/L or mg P_2O_5/L)

(mg P/L) x 3.066 = mg PO_4/L

(mg P/L) x 2.291 = mg P_2O_5/L

9.4 Accuracy

9.4.1 ICV, CCV, LCS % Recoveries

$$\%\,R = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

9.4.2 Matrix Spike % Recovery

9.5 Precision for MD or LCD RPD

$$\text{RPD} = \frac{|\text{orig.sample value} - \text{dup.sample value}|}{\left[\frac{\text{orig.sample value} + \text{dup.sample value}}{2}\right]} \times 100$$

10.0 POLLUTION CONTROL

It is Eurofins policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

10.1 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to UP-WM-001.

The following waste streams are produced when this method is carried out.

- The neutralized sample waste from this procedure will enter the ‘Wastewater Wastestream’.

11.0 METHOD PERFORMANCE CRITERIA

Refer to Sections 1, 6, 7 and 8.

12.0 REFERENCES

Refer to Section 1.0

13.0 ATTACHMENTS

Attachment 1: Sample Analysis on AQ700
Attachment 2: Example: rAIPD-T Maintenance Log
Attachment 3: Example: AQ Baseline
Attachment 4: Example: Daily (Morning) Tasks
Attachment 5: Example: Daily (Evening) Tasks
Attachment 6: Example: Weekly Maintenance

14.0 REVISION HISTORY

- Revision 30 updated on 03/20/24
- Adding a methodSection 1.0 Add reference to 365.1 Rev. 2.0
- Section 4.0 Updated equipment and supplies for AQ700
- Section 5Updated reagents for 365.1
- Sections 5.2.5.1, 5.2.5.2, and 5.2.5.3 Added AQ700 parameters
- Section 7.1 Added 365.1 criteria
- Section 7.5 Add maintenance for AQ700
- Section 7.6 Add reference to attachment 1 for Sample Analysis on AQ700

Attachment 1.

Sample Analysis on AQ700 (CHI-22-12-189/A-3/24)

Sample Analysis on AQ700

Perform “Daily Startup” in the maintenance and setup tab
Fill reagent wedge(s) with reagent(s) as listed in Table 1 and place the wedge(s) into the reagent tray.

TABLE 1		
Method	**Reagent Wedge #**	**Reagent**
TKN	5	TKN Working buffer
	6	Working Salicylate nitrofericyanide
	7	Sodium hypochlorite
	22	TKN synthetic blank matrix
Nitrite	16	Sulfanilamide-nedd
Phosphorus	3	Working color reagent
	4	Working ascorbic acid
Phenol	13	4-Aminoantipyrine (AAP)
	14	Potassium Ferricyanide
Nitrate-Nitrite	2	NOx Diluent
	16	Sulfanilamide-nedd
Ammonia	3	Salicylate
	4	DCI
	21	Calibration diluent

Double-click “scheduling” in the AQ700 software, and select a tray number and reagent set. Name the tray with today’s date, [test name], and a letter to designate the run number. See Table 2 for information.

TABLE 2		
Method	**Reagent Set**	**Test Name**
TKN	1	TKN022824A
Nitrite (N02)	1	031524N02A
Phenol	1	Phenol022924A
Phosphorus	2	ophos022824a Tphos022824a
Nitrate (N03)	1	031524N03A
Ammonia	1	022824NH3A

Starting with cup 1, add the QC into the schedule. (ICV, ICB, MB, LCS) Then, scan in the samples, including MS/MSD.

NOTE: there is no need to add any CCVs/CCBs to the schedule. The software automatically inserts them every 10 samples.

Highlight all of the QC and samples in the schedule and select the correct test from available tests (See Table 3). To add any dilutions, highlight the desired sample(s), select the dilution factor, and click [test] for a second time. This will add an auto-dilution to any highlighted samples.

TABLE 3	
Method	**Test Name**
TKN	TKN
Nitrite	N02
Phenol	Phenol
Phosphorus	oP
Nitrate	Nitrate
Ammonia	NH3

Remove one of the four trays from the instrument, and using 2mL sample cups. Load the tray according to the schedule generated above.

NOTE: See Table 4 for respective cups that he CCV and High calibration standard should be placed in.

TABLE 4		
Method	**Cup Positions**	
TKN	103	104
Nitrite	88	89
Phenol	105	106
Phosphorus	105	106
Nitrate	105	106
Ammonia	105	106

On the “run” screen, select “tray placement.” Select the tray that corresponds to the tray loaded above. Select the schedule associated with the tray as well as reagent set (Table 5). Select “okay.”

TABLE 5	
Method	**Reagent Set**
TKN	1
Nitrite (N02)	1
Phenol	1
Phosphorus	2
Nitrate (N03)	1
Ammonia	1

On the “run” screen, select auto start. On the pop-up that follows, check any necessary boxes (perform calibration, replace cuvettes, etc.) and select “okay”
The next pop up will only appear if an auto-calibration was requested. Ensure the correct method is checked, and click “okay.”
When the run is complete, double click “data review,” and select the desired tray. If dilutions are required, add the necessary dilution factor by selecting “dilution factor”

and press “okay.” Highlight the desired sample, and select “auto dilution.” This will add the dilution factor, as well as reschedule the sample. Be sure to reschedule necessary CCVs and CCBs by highlighting them and selecting “reschedule.” Once analysis is truly complete, select the tray in the “data review” tab and click “accept all.” The software will ask if the user is sure. Click “yes” and the software will generate a CSV file with the results. Name the file and save it into the “out” folder. Copy the CSV file, and paste it into the test (Table 6) Tals transfer folder.

TABLE 6

Method	TALS Transfer Folder	Import Path
TKN	TKN	\\corptalsapp16\500-CH-RawData\WetChem\Seal3\SM4500_TKN_H(TKN_DIL)
Nitrite	N02	\\corptalsapp16\500-CH-RawData\WetChem\Seal3\SM4500_NO2_B(NO2)
Phenol	Phenol	\\corptalsapp16\500-CH-RawData\WetChem\Seal3\420.4(PhenolTR)
Phosphorus	Phosphorus	\\corptalsapp16\500-CH-RawData\WetChem\Seal3\4500_P_E(TPHOS) \\corptalsapp16\500-CH-RawData\WetChem\Seal3\4500_P_E_Ortho(Ortho1)
Nitrate	Nitrate	\\corptalsapp16\500-CH-RawData\WetChem\Seal3\4500NO3F(NO3_NO2)
Ammonia	Ammonia	\\corptalsapp16\500-CH-RawData\WetChem\Seal3\SM4500NH3_G(350.1)

Under “reporting” in the AQ software, select the tray, and generate the “Eurofins 1.0” report. On the right side of the page, the software will present a preview of the document. Right click on the document and select “print.” Print the report to a PDF and save it into the [test] folder (wetchem – raw data for printing –[test]) with the date of analysis, [test], and the letter designating the run number (Table 7).

TABLE 7

Method	Test Folder	EX: Name
TKN	TKN	TKN022824A
Nitrite	N02	031524N02A
Phenol	Phenol	Phenol022924A
Phosphorus	Phosphorus	ophos022824a Tphos022824a
Nitrate	Nitrate	031524N03A
Ammonia	Ammonia	022824NH3A

Attachment 2.

Example: Maintenance Log

Eurofins Chicago
rAPID-T-4: Model 4600 (SN: 4660-1073)
Instrument Maintenance Log

Page No._____

Daily Maintenance:	Initial	Initial	Initial	Initial	Initial	Initial	Initial
Check/Fill Water Container							
Check Waste Container							
Check Syringe for Air Bubbles							
System Check – Start of Day							
Shut Down Routine – End of Day							

Non-Routine Maintenance:*	Date	Initials	Maintenance Details	Return to Control
Change Syringe				
Change Probe				
Change Lamp				

Comments:_____

*Any Maintenance/Repair/Part Replacement performed that is not listed above must be documented. Note: Vendor maintenance records are to be attached to the logbook page.

Reviewer Signature:_____ Date:_____

CHI-22-12-165/A-09/19

Attachment 3.

Example: AQ Baseline

AQ700 Water Baselines

SEAL Analytical

Software version:	2.5.01A43
User name:	Kaitlin
Time and Date:	2024-03-14 07:22:29

Filter Number	Filter	Previous water baselines	Current Water baselines
1	405	4.7341 v (Gain = 229)	4.7388 v (Gain = 229)
2	450	4.7207 v (Gain = 192)	4.7259 v (Gain = 192)
3	480	4.6852 v (Gain = 151)	4.6919 v (Gain = 151)
4	505	4.6893 v (Gain = 190)	4.6958 v (Gain = 190)
5	520	4.6865 v (Gain = 174)	4.6948 v (Gain = 174)
6	546	4.7177 v (Gain = 202)	4.7250 v (Gain = 202)
7	578	4.6708 v (Gain = 180)	4.6793 v (Gain = 180)
8	660	4.7022 v (Gain = 189)	4.7127 v (Gain = 189)
9	880	4.7551 v (Gain = 209)	4.7631 v (Gain = 209)
10	Dark	0.0273 v	0.0273 v
Time & Date		**2024-03-13 10:39:13**	**2024-03-14 07:20:13**

Attachment 4.

Example: Daily (Morning) Tasks

SEAL Analytical

AQ700 Daily (Morning) Tasks

	Daily (Morning) Tasks	
☑	Empty and Refill Wash Water Reservoir	
☑	Empty the Waste Container	
☑	Replace Reaction Segments as Required	
Maintenance Menu		
	☑	Observe movements during initialization • Movements should be smooth and they should be the same each initialization
	☑	**DILUTER:** Prime both Syringes (5-10 times) • Verify no air remains in syringes and they are operating smoothly.
	☑	**DILUTER:** Check operation of the Probe Wash assemblies • Turn on Waste Pumps and Wash Valve • Verify water movement through both chambers
	☑	**CUVETTE FUNCTIONS:** Perform 1-5 Auto Washes • Observe Wash Bath is Filling and Clean
	☑	**SPECTRO**: Perform 1 Auto Wash. Run Water Baselines. • Auto-gain baselines should have gain results within ± 2 from day to day operations.
☑	Inspect reagents for particulates or excessive color. Filter or replace reagents as needed. Check the method documents for information on reagent stability and symptoms of reagent degradation.	
☑	Cadmium Coil checks as required. See Cadmium Coil Care section of the Nitrate + Nitrite method documentation	

Attachment 5.

Example: Daily (Evening) Tasks

SEAL Analytical

AQ700 Daily (Evening) Tasks

	Daily (Evening) Tasks
☑	Place Cuvette Cleaning Solution in Reagent Position 1. Maintenance and Setup – Extra Wash
☑	Zero Segments –Maintenance and Setup, Zero Segments and discard the used reaction segments
☑	Discard used Sample Cups
☑	Empty the Waste Container
☑	Empty the Wash Water Reservoir
☑	Put Reagent Tray into the refrigerator for overnight storage
☑	If any spills on the reagents tray, clean the tray by removing the reagent wedges, wiping up spills and condensate in the tray and wiping the bottom of the wedges.
☑	If any spills on the carousel, clean the reaction carousel by removing reaction segments and wiping spills in and around the carousel
☑	Archive completed runs in Data review

Attachment 6.

Example: Weekly Maintenance

SEAL Analytical

AQ700 Weekly Maintenance

	Weekly Tasks
☑	Record and compare water baseline voltages to monitor lamp stability. If gains change suddenly (within 2 weeks) by more than 5, the lamp may need to be replaced.
☑	Clean Sampler Wash Bath
☑	Clean Aspiration Wash Bath
☑	Clean Cadmium Reduction Well
☑	Inspect Sampler Probe – Straight, Clean, Not Dripping
☑	Inspect Aspiration Probe – Straight, Clean, Not Dripping

TITLE: Wet Chemistry
Specific Conductance and Salinity

Approvals (Signature/Date):

Logan Poracky 8/2/24
Logan Poracky Date
Supervisor, Wet Chemistry

Chris Hoham 8/2/24
Chris Hoham Date
Env. Health & Safety Coor.

Nicole Berg 8/2/24
Nicole Berg Date
Quality Assurance Manager

Paul Kolarczyk 8-2-24
Paul Kolarczyk Date
Inorganic Technical Director

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1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) is used to determine the specific conductance of aqueous sample matrices, and to determine salinity by the electrical conductivity method. This SOP was written using EPA-570/9-82-020 Method 120.1; SW-846 Method 9050A; and Standard Methods 2510B-97 and 2510 B-2011 for specific conductance, and Standard Methods 2520A-93, 2520B-93 and SM 2520 B-2021 as references for salinity. Standard Methods 2020B was used to confirm QC requirements. Additionally, Eurofins Chicago uses conductance-to-salinity conversion tables provided by Amber Scientific and verified mathematically in-house. The table and in-house calculations are on file at the laboratory.

On occasion, clients request slight modifications to this SOP. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP) and authorized via laboratory signature approval; and amended to the data packages case narrative.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

Not Applicable.

1.1.2 Demonstration of Capability

Before the laboratory may institute a new method and begin reporting results, the laboratory shall confirm that it can properly operate the method. A demonstration of capability is performed whenever there is a change in instrument type, method or personnel. An Initial Demonstration of Capability (IDOC) must be thoroughly documented and approved by the Department Manager/Supervisor and QA Manager prior to independently analyzing client samples. All associated documentation must be retained in the QA Department and in the Analyst Training files. For additional details on the demonstration of capability procedures followed, refer to the laboratory SOP, *UP-QA-QAM, Quality Assurance Manual, Sections 19.4.2 and 19.4.3.*

1.1.3 Reporting Limits

1 µmhos/cm.

1.1.4 Definitions

Refer to Section 3.0 of the Laboratory's Quality Assurance Manual (UP-QA-QAM).

1.2 Summary of Method

Conductivity is a numerical expression of the ability of an aqueous solution to carry an electrical current. This depends on the presence of ions, their total concentration, mobility, valence and relative concentrations as well as the temperature of measurement. Solutions of most inorganic acids, bases and salts are relatively good conductors. Molecules of organic compounds that do not dissociate in aqueous solution conduct a current poorly, if at all. Conductance is expressed in units of mhos. A more convenient unit in water analysis is micromhos (µmhos). Specific Conductance is frequently used as an indicator of well-purging stability when sampling monitoring

wells. Consecutive stable conductivity readings are an indication that the well has been purged sufficiently that a representative sample may be drawn.

The physical measurement made in a laboratory of conductivity is usually that of resistance. The resistance of a conductor is inversely proportional to its cross section and directly proportional to its length. This resistance depends on the characteristics of the conductivity cell used. Practical electrodes measure a given fraction of the specific resistance, the cell constant, C.

$$C = \frac{\text{mesured resistance,Rm}}{\text{specific resistance,Rs}}$$

The reciprocal of resistance is conductance.

$$k_s = \frac{1}{R_s} = \frac{C}{R_m}$$

Where:
k_s is the specific conductance

2.0 INTERFERENCES

- None, but be cautious of oily samples, as they will coat the cell.
- Temperature will affect conductance. See below.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Lab Specific Addendum to the CSM, and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coat and closed-toe, nonabsorbent shoes are a minimum.

3.1 Specific Safety Concerns or Requirements

All samples should be handled with care due to the uncertainty of the properties and contents involved.

3.2 Primary Materials Used

A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

4.0 EQUIPMENT AND SUPPLIES

- Amber Scientific Model 1056 Conductivity Meter, with gold and platinum probes
- Mantech Automax 401 Robot
- DI Water Bottle
- Test tubes and rack

- Volumetric flasks and pipets, when standards are made
- Desiccator
- Oven at 103-105°C

5.0 REAGENTS AND STANDARDS

5.1 Stock Standards

5.1.1. Stock standards are purchased from an approved vendor. If no expiration date is provided, the stock standard solutions may be used for up to one year from open date and must be replaced sooner if verification from an independent source indicates a problem.

5.2 Intermediate / Working Standards

5.2.1. Intermediate / Working standards are prepared as dilutions from the stock standards. Intermediate / working standard solutions shelf life and are stored according to table below.. The intermediate / working standard solution must be replaced if verification from an independent source indicates a problem. Refer to the LIMS standards and reagents module for further details on preparation of intermediate / working standard solutions.

Reagent	Shelf Life	Storage Requirements
1413 µmhos/cm Standard*	1 year	None
718 µmhos/cm Standard*	1 year	None
147 µmhos/cm Standard	1 year	None
15 µmhos/cm Standard	1 month	None
10 µmhos/cm	3 month	None
100 µmhos/cm	1 year	None
1000 µmhos/cm	1 year	None
50000 µmhos/cm	1 year	None
* The dried KCl must be completed for 24 hours at 105°C		

6.0 CALIBRATION (NON-DAILY)

Not Applicable.

7.0 PROCEDURE

7.1 Quality Control Checks

Quality Control	Frequency	Control Limit
Matrix Duplicate (DU)	1 in 10 samples, per range	≤ 20 RPD

Drinking water samples must have a DU performed for every 10 or fewer samples, in addition to any non-drinking water QC that may have been done.

7.2 Sample Preservation and Handling

Holding time, preservation techniques and sample container may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client request. Listed below are the holding times and the references which include container and preservation

requirements for compliance with the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA).

	Holding Time	Reference	Preservation
SDWA	28 days	EPA 570/9-82-002	Cool, ≤ 6˚C
CWA	28 days	40 CFR Part 136	Cool ≤ 6°C

Note: Method 120.1 states that if the analysis cannot be done with 24hrs. The sample should be filtered through a 0.45 filter and stored at 4ºC, but the Federal Register gives 28 days as the holding time. Eurofins Chicago follows the 28-day guidance.

7.3 Sample Preparation

Solid samples logged with a DI Leach preparation

7.4 Calibration / Standardization

7.4.1 Analytical Sequence

When using the Amber Scientific Model 1056 Conductivity Meter, follow this sequence. Standard Methods only requires standardization of the meter/probe with the 1413 µmhos/cm standard. Eurofins Chicago brackets all reported sample readings with the closest of the following:

Calibration Controls	Sequence	Control Limits
Cell constant	Daily, prior to analysis	≤ 1.003 (see 7.4.2)
ICV / LCS 10 µmhos/cm 100 µmhos/cm 1000 µmhos/cm 50000 µmhos/cm	ICV after calibration; LCS per batch / per range used	 ± 2% (9.8-10.2) ± 2% (98-102) ± 2% (980-1020) ± 2% (49000-51000)
	CCV after every 10 Samples / per range used	± 2% (14.6-15.2) ± 2% (144.1-149.9) ± 2% (704-732) ± 2% (1385-1441)

When using the Mantech Automax 401 Robot, the instrument calibrates using

Calibration Controls	Sequence	Control Limits
Calibration 15.0 µmhos/cm 147 µmhos/cm 718 µmhos/cm 1413 µmhos/cm	Daily prior to analyis	

ICV / LCS 10 µmhos/cm 100 µmhos/cm 1000 µmhos/cm 50000 µmhos/cm	ICV after calibration; LCS per batch / per range used	 ± 2% (9.8-10.2) ± 2% (98-102) ± 2% (980-1020) ± 2% (49000-51000)
Blank (cell constant)	Daily prior to analysis of samples	≤ 1.003 (see 7.4.2)
CCV (718 µmhos/cm)	CCV after every 10 samples	± 2% (704-732)

7.4.2 Cell Constant

With the power on and the cell connected, turn the function switch to A.T.C. "ON" and the range switch should be indicating that the meter is in the “D” range. Using 3-aliquots of 718 micromho Standard I, Rgt. 5.2, dip the cell into the first aliquot allowing the temperature to stabilize. Agitating the cell in the solution helps the stabilization and gets rid of any air bubbles. Take the cell out and shake off any excess solution that may cause any carry over. Place the cell in the second aliquot and repeat the process. Put the cell in the third aliquot and at this point a reading may be taken. The reading will be the most accurate if taken as soon as the cell is dipped into the third sample. Some readings may drift due to gases or other impurities absorbed from the atmosphere. At this point, the meter should read 0.718 millimhos. If the meter needs to be adjusted, take a small screwdriver and set the display to read 0.718.

The Mantech Automax 401 Robot dips the probe into the sample cup 3 times before taking a reading on the sample for conductivity.

Obtain the day’s reading of the laboratory DI water from the water monitoring program performed by the QA department. If the QA department has not tested the conductivity on the day of this analysis, calibrate the meter with the 15 µmho/cm standard and read the DI water. It must be ≤ 2 for the cell constant to calculate as acceptable. Use the following equation to determine the cell constant.

$$\text{Cell Constant} = \frac{(\text{Cond. of KCl Std.} + \text{Cond. of DI water})}{\text{True Value of KCl Std.}}$$

If the result is ≤ 1.003, no action should be taken, except to record this in the data book. Again, this will be true as long as the DI water conductance is ≤ 2 µmho/cm.

7.5 Preventive Maintenance

Rinse the cell between samples with Milli-Q water and dispose of excess solution by shaking the cell. Do not wipe or touch the cells. Store the cells dry.

The Amber Scientific Model 1056 Digital Conductivity Meter requires no routine maintenance, but the ***ATC function should be verified annually*** using the following protocol:

First check the ATC against an NIST certified thermometer and note any correction factor.

Prepare a water bath at <10°C. Place three test tubes containing the 718-uµmho standard in the bath and allow them to come to equilibrium. After two 718 µmho rinses of the cell, read and record the conductivity of the cooled standard, ensuring that the ATC is on. (The switch is on the back of the meter.) Slowly warm the standards to 25°C and then to ~35°C, reading and

recording the conductivity of the standard at each temperature. The readings should be approximately the same at all temperatures. Switch off the ATC while the probe is in the warmed standard, and the conductivity should change. Record your findings in the IMB book. Remember to turn the ATC back on. If this test fails to produce the expected result, contact the manufacturer for instructions.

7.6 Sample Analysis

7.6.1 Cell Specifications

The 515 Dip Cell has gold (Au) plated plates which have less of a tendency to carry over solution from one measurement to the next. The linearity of the gold cell is not guaranteed above 2000 micromhos.

The 525 Dip Dell is coated with platinum (Pt). This cell has a little more problem with carry over and is used only for samples >2000 µmhos/cm. Use the platinum cell for salinity samples, reverting to gold in the conductivity is <2000 µmhos/cm.

The Probe (Au or PT) used for the analysis of each sample is documented in TALS.

7.6.2 Sample Size

The cell must be immersed a minimum of 1 1/4 inches for proper measurement. Approximately 30 mLs of sample is divided into 10 mL aliquots in culture tubes for analysis for the Amber Scientific meter.

The Mantech Automax 401 Robot requires approximately 30ml in a vial for the auto-sample rack.

7.6.3 Range Calibration Verification

Initially, read all samples after the 718 µmhos/cm standard. Any samples that are closer in conductivity to another one of the standards will not be reported from this reading, but will be re-read after the closer standard. Three aliquots of every sample need to be poured into the appropriately marked test tubes. An additional one will be poured as a duplicate. As before, place the cell in the first two tubes to equilibrate and take the reading from the third tube. (It is not necessary to dip into all three test tubes of samples that are found to be out of range, but record the screening value with a comment that it must be re-read.) Bracket each 10 or fewer sample readings with readings of the 718 µmhos/cm standard.

Segregate the remaining screened samples according to which of the three remaining standards each most closely approximates. Read each group, again bracketing every 10 or fewer samples with readings of the most appropriate standard according to the following table. The meter must first be calibrated in each new Standard range by following the procedure given above for the 718 µmhos/cm Standard.

NOTE: All samples may be prescreened prior to calibration, since the meter holds calibration quite well, and not all Standard ranges may be needed. *The cell constant can be determined from whichever Standard is used first.*

NOTE: While the cell is in the first two tubes, the range on the meter can be better judged. Pick the range that will give you the most digits for your result. If you have turned the range too high or too low, a "1" will appear indicating that the range you have picked does not have that

amount of resolution required to read that specific sample. Also, document the range in which the third reading was taken.

NOTE: Standards and samples should be close to room temperature before readings are taken. The meter compensates for temperature but most accurate results are gained if standards and samples are close to room temperature. **Do not leave samples out of the cooler longer than necessary to bring the samples to room temperature and to perform the analysis. It is important to maintain the integrity of the samples for all testing protocols.** A warm water bath may be used to more rapidly bring samples to approximately room temperature.

NOTE: Be sure to use the platinum cell for, and only for, samples over 2000 µmhos/cm.

Initial (screening) reading in µmho/cm	Concentration of calibration standard µmho/cm
< 81	14.9 with gold cell
82-432	147 with gold cell
433-1066	718 Report from above (two rinses)
1067-2000	1413 with gold cell
>2000	1413 using platinum cell

Note: For the Mantech Automax 401 Robot the samples do not need to be prescreened.

7.7 Documentation

7.7.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

7.7.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

7.7.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs are scanned and attached to the Documents section in the LIMS analytical batch.

7.7.4. Record all sample results and associated QC directly into LIMS. Level I and Level II reviews are performed in LIMS.

Examples of items included in the above reviews are as follows:

- QC data are outside the specified control limits for accuracy and precision
- Samples having unusually high results
- Samples exceeding a known regulatory limit
- Raw data indicating some type of contamination or poor technique
- Transcription errors

The data from the Mantech Automax 401 Robot is transferred into the LIMS system using the MantechTransferApp. The raw data is printed to a pdf and attached to the analytical batch.

8.0 QUALITY CONTROL

8.1 QC Summary

8.1.1 One DU is performed per matrix per 10-sample analytical set. Results must agree within 20 RPD.

8.2 Corrective Action

When an out of control situation occurs, the analysts must use his/her best analytical judgment and available resources to determine the corrective action to be taken. The out of control situation may be caused by more than one variable. The analyst should seek the assistance of his/her immediate supervisor, QA personnel, or other experienced staff if he/she is uncertain of the cause of the out of control situation. The test must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out of control situation should be reanalyzed. Out of control data must never be released without approval of the supervisor, project manager, QA personnel or the lab director.

Steps that MUST be taken when an out of control situation occurs:

- demonstrate that all the problems creating the out of control situation were addressed;
- document the problem and the action which was taken to correct the problem on the data review checklist and write a Non-Conformance Memo (NCM);
- receive approval (signature) of the supervisor, QA personnel, or the Laboratory Director prior to the release of any analytical data associated with the problem.

QC Indicator	Suggested Corrective Actions [1]
Cell Constant	• refer to instrument manual or contact manufacturer
ICV / LCS	• repeat to verify proper preparation; • check for instrument drift; clean gold or platinum dip cell if needed • restandardize with existing standards, reanalyze; • check reagents/solutions and prepare fresh if necessary; • prepare new stock and/or working standards and recalibrate; and • document all situations on the data review checklist.
DU	• the sample must be reprocessed and reanalyzed unless the sample concentration is <5 times the Reporting Limit, then the ± Reporting Limit rule applies; • if the reanalysis is within the control limits, the second duplicate value is reported; • if the reanalysis is still outside of the control limits, the closer two results are generally reported but are approved by your supervisor
CCV	• repeat CCV to verify proper preparation; • prepare new CCV from original stock; • check for cell drift; clean gold or platinum dip cell if needed • recalibrate and repeat all samples since the previous in control CCV; • never dispose of any samples until you are sure that all QC are within their designated control limits; • document all situations on the data review checklist.

[1] Client-specific QAPs may specify corrective actions that supersede those suggested above.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 The meter reports results using either millimhos or micromhos. When reporting results from ranges A - C, the results are in micromhos. When reporting results from ranges D - F, the results are in millimhos, and the results must be multiplied by 1000 to convert to micromhos/cm. The final results are reported as micromhos/cm (µmhos/cm).

Example: The first standard reading is 0.718 millimhos.

0.718 x 1000 = 718 micromhos (Conversion Factor: 1 millimho = 1000 micromho)

Although the temperature is not shown in Analyst Desktop, the final report to the client will express the test name as "Specific Conductance (25°C)".

9.1.1 To report practical salinity, compare the observed conductivity to the salinity table obtained from Amber Science, Inc., Eugene, OR.

9.2 Accuracy

9.2.1 ICV/CCV ±2%

The µmhos/cm acceptance range for each standard is listed in section 7.4.1.

9.3 Precision

9.3.1 Matrix Duplicate (RPD)

$$\frac{|\text{Orig.Sample Value} - \text{Dup.Sample Value}|}{\left[\frac{\text{Orig.Sample Value} + \text{Dup.Sample Value}}{2}\right]} \times 100$$

10.0 POLLUTION CONTROL

It is Eurofins policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

10.1 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to UP-WM-001.

The following waste streams are produced when this method is carried out.

- Waste from this procedure will enter the "waste water" wastestream.
- Single component standards will be turned over to the EHSC or waste technician for disposal.

11.0 METHOD PERFORMANCE CRITERIA

Refer to Sections 1, 6, 7 and 8.

12.0 REFERENCES

Refer to Section 1.0

13.0 ATTACHMENTS

NA

14.0 REVISION HISTORY

- Revision 26 updated on 08/02/24
- Annual Review
- Throughout added ManTech
- Section 1.0 added reference to SM 2520 B-2021

TITLE: WET CHEMISTRY
Total Acid Soluble and Reactive Sulfide

Approvals (Signature/Date):

Paul Kolarczyk — 5/23/23
Paul Kolarczyk — Date
Supervisor, Wet Chemistry

Chris Hoham — 5/23/23
Chris Hoham — Date
Env. Health & Safety Coor.

Nicole Berg — 5/23/23 — NMB 5/23/23
Nicole Berg — Date
Quality Assurance Manager

Ray Shock, III — 5/23/23
Ray Shock, III — Date
Technical Director

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1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) describes the procedure to determine the concentration of sulfides in drinking, surface and saline waters and of acid soluble and reactive sulfides in solid wastes and soils. . This SOP was written using the following references:

- SW-846, 3rd Edition, Method 9030B (distillation) and 9034 (titration) (for acid extractable analysis).
- Standard Methods 4500-S^{2-}F-00, 4500-S^{2}-F-2011, and 4500-S^{2}-F 23rd ED with optional 4500-S^{2-}C-00.
- SW-846, 3rd Edition, Section 7.3.4.2 for Reactive Sulfide in solid waste. . This method has been withdrawn by the US EPA, but it is frequently requested by Eurofins Clients and therefore kept in this SOP, but it will be phased out in favor of 9030B/9034 for all solids.
- Extraction by Method 9030B is not applicable to oil, oily wastes, or multiphasic matrices. Contact the supervisor or PM in the event such a sample is received. .

On occasion, clients request slight modifications to this SOP. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP), authorized via laboratory signature approval, and mentioned in the data package's case narrative.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL), referred to as the detection limit (DL) in NELAC documents, is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants" with additional details are provided in the Eurofins Corporate SOP, *NDSC-QA-SOP42091, Detection and Quantitation Limits* and the Eurofins Chicago SOP, *UP-QA-017, Method Detection Limit Studies.* MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; the MDL will be performed and verified on an annual basis verifying the Lower Limit of Quantitation (LLOQ) for the method.

1.1.2 Demonstration of Capability

Before the laboratory may institute a new method and begin reporting results, the laboratory shall confirm that it can properly operate the method. A demonstration of capability is performed whenever there is a change in instrument type, method or personnel. An Initial Demonstration of Capability (IDOC) must be thoroughly documented and approved by the Department Manager/Supervisor and QA Manager prior to independently analyzing client samples. . All associated documentation must be retained in the QA Department and in the Analyst Training files. For additional details on the demonstration of capability procedures followed, refer to the laboratory SOP, *UP-QA-QAM, Quality Assurance Manual, Sections 19.4.2 and 19.4.3.*

1.1.3 Reporting Limits (LLOQ)

Reporting Limits (LLOQ) are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. The laboratory maintains reporting limits that are set higher than the MDL. Wherever possible, reporting is limited to values approximately 3-5x the respective MDL to ensure confidence in the value reported. Reporting limits and MDLs values are easily accessible in TALs

Note: Reporting limits will vary depending on sample volume/size, dilution factors, dry weight reporting (soils/waste).

1.1.4 Definitions

Refer to Section 3.0 of the Laboratory's Quality Assurance Manual (UP-QA_QAM).

1.2 Summary of Method

For acid-soluble sulfide or reactive sulfide samples, separation of sulfide from the sample matrix is accomplished by the addition of acid to the sample in a closed system in which the hydrogen sulfide (H_2S) formed is carried by a nitrogen stream into a zinc acetate gas scrubbing bottle, where it is precipitated as zinc sulfide.

The sulfide in the zinc sulfide precipitate is oxidized with a known amount of iodine, in excess of that required by the sample. Then the excess iodine is determined by titration with a standard solution of sodium thiosulfate until the blue iodine starch complex disappears. Quantitation is based on the volume of sodium thiosulfate required.

Water samples may be treated for interferences or concentrated by precipitation, filtration, and re-suspension, or may be titrated directly.

This method provides only a semi-quantitative determination of sulfide compounds considered "acid-insoluble" (i.e., CuS; SnS_2) in solid samples.

Note: The US EPA has determined that the method for reactive sulfide is unreliable, and recommends that laboratories analyze samples for total sulfide instead. . This is the practice at Eurofins Chicago for any water samples that are received for reactive sulfide. . However, Eurofins Chicago does follow SW 846 Section 7.3.4.2 for reactive sulfide in soils and wastes.

2.0 INTERFERENCES

- Prior to preservation and precipitation of the sulfide in water samples by zinc acetate, the sample should not be agitated.
- The iodometric method suffers interferences from reducing substances that react with iodine, including thiosulfate, sulfite, and various organic compounds, both solid and dissolved.
- Eliminate interferences due to sulfite, thiosulfate, iodide and many other soluble substances (not including ferrocyanide) by first precipitating zinc sulfide, then removing the supernatant and replacing with deionized water. Water samples, when high concentrations of thiosulfate is present (higher than 10 mg/L), may have a "retard color formation". Iodine concentrations higher than 2 mg/L may diminish color (wastewaters).

- Reduced sulfur compounds, such as sulfite and hydrosulfite higher than 10 mg/Kg, decompose in acid and may form sulfur dioxide. This could create a positive interference and false high values. SW-846 states that adding formaldehyde to the scrubber solution can eliminate this interference but due to employee safety considerations, Eurofins Chicago does not use formaldehyde. Sulfite test strips will be used to determine if sulfite is present in the solid samples prepared by method 9030B.
- Oils, oily wastes, or multiphasic samples are not appropriate for the protocols in this SOP.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual, Lab Specific Addendum to the CSM, and this document. . This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coat and closed-toe, nonabsorbent shoes are a minimum.

3.1 Specific Safety Concerns or Requirements

Sodium Sulfide will form Hydrogen Sulfide (H_2S) gas if combined with water, moisture, or strong acids. Inhalation of H_2S gas can cause headache, dizziness, nausea, and unconsciousness and potentially death.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. . **NOTE: This list does not include all materials used in the method. . The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table. .** A complete list of materials used in the method can be found in the reagents and materials section. . Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and Symptoms of Exposure
Iodine	Poison Corrosive Oxidizer	0.1 ppm-Ceiling	Vapors severely irritate and can burn the mucous membranes and respiratory tract. . Liquid contact may cause blistering burns, irritation, and pain. Vapors may be severely irritating to the skin. Vapors are severely irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Material (1)	Hazards	Exposure Limit (2)	Signs and Symptoms of Exposure
Sodium Hydroxide	Corrosive	2 mg/m^3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sodium Sulfide	Corrosive	10 ppm-TWA 15 ppm-STEL	Will form Hydrogen Sulfide (H_2S) gas if combined with strong acids. . Inhalation of gas (H_2S) may be fatal. Symptoms include painful conjunctivitis, headache, nausea, dizziness, coughing and, in extreme cases, pulmonary edema and possible death. Irritant. Contact with skin can produce serious caustic burns with painful inflammation and possible destruction of tissue. Inflammation, tearing and pain may be expected. Severe contact can cause destruction of tissue.
Sulfuric Acid	Corrosive Oxidizer Dehydrator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 EQUIPMENT AND SUPPLIES

- Westco Easy-dist jr. sulfide glassware
- 20-place block digester
- 5 mL volumetric pipets
- 10 mL disposable pipettes
- Top-loading balance
- Digital buret
- Nitrogen gas
- Glass fiber filters
- Extension funnel
- Class A graduated cylinders – various
- Sulfite test strips – sensitive to 10 mg/L

5.0 REAGENTS AND STANDARDS

All reagents are prepared with Type II Deionized Water, unless otherwise specified, in class A volumetric flask. . Use reagent grade chemicals.

5.1 Iodine Solution, ~0.025 N

A purchased pre-made Iodine solution may be used or the solution may be prepared as follows. Dissolve 20 to 25 grams potassium iodide in ~500 mL DI water in a 1.0 L Class A volumetric flask. Add 3.2 grams iodine. After the iodine has dissolved, dilute to volume and standardize daily against standard sodium thiosulfate using starch indicator. (See Section 7.4.1)

- Life of Reagent: 1 year
- Storage Requirements: Store in dark bottle 15 - 30°C.

5.2 Hydrochloric Acid, Concentrated

Purchased from a chemical vendor.

- Life of Reagent: 5 years
- Storage Requirements: none

5.3 6 N Hydrochloric Acid

Slowly add 500 mL of concentrated hydrochloric acid to a 1.0 L volumetric flask containing ~450 mL DI water. Cool and dilute to volume with DI water.

- Life of Reagent: 1 year
- Storage Requirements: none

5.4 Sodium Thiosulfate, ~0.025 N

Using an analytical balance capable of measuring 0.1 mg, weigh out 6.205 grams sodium thiosulfate [$Na_2S_2O_3 \cdot 5H_2O$] and quantitatively transfer to a 1.0 L Class A volumetric flask. Add 1.5 mL 6 N sodium hydroxide (NaOH) or 0.4 grams solid sodium hydroxide and dilute to just under 1.0 L with DI water. Standardize upon preparation with potassium bi-iodate solution as follows:

Dissolve 2 grams potassium iodide in an Erlenmeyer flask with 150 mL DI water. Add a few drops of concentrated sulfuric acid and 10.0 mL of Standard Potassium Bi-iodate solution (Section 5.8) using a volumetric pipette. Dilute to ~200 mL. Titrate with Standard Sodium Thiosulfate until a pale straw color is reached. Add starch indicator and continue titrating to the first disappearance of the blue color. Determine the Normality of the Sodium Thiosulfate using the following calculation:

$$(N)\,(V) = (0.025\ N)\,(10.0\ mL)$$

Where:
N = Normality of Sodium Thiosulfate
V = volume of Sodium Thiosulfate
Standardize in triplicate and use the average value in calculating the Normality.

- Life of Reagent: 1 year
- Storage Requirements: none

5.5 Starch Indicator

Dissolve 2 g laboratory grade soluble starch and 0.2 g Salicylic Acid, as a preservative, in 100 mL hot DI water. Alternatively, this can be purchased from a vendor or a powdered starch form can be used.

- Life of Reagent: 1 year
- Storage Requirements: refrigerate

5.6 Sulfide Stock 1, ~200 mg/L

Dissolve 1.500 grams of sodium sulfide [$Na_2S \cdot 9H_20$] in a 1.0 L Class A volumetric flask with DI water. Add 10 mL of 0.5 M Zinc Acetate solution (Rgt. 5.11) as a preservative and bring to volume

with DI water. The “true value” is determined upon preparation by averaging the titration results of 3 aliquots. Using a 5.0 mL volumetric pipette, add 5.0 mL of well-mixed Stock Sulfide Solution to ~100 mL and titrate as for a sample (See section 7.4.1). Calculate the sulfide concentration using 5 mL as the sample volume. Repeat 2 times and average the concentrations for use as the “true value”. .

- Life of Reagent: 1 year
- Storage Requirements: store in amber bottle

5.7 0.25 N Sodium Hydroxide

Dissolve 10 grams of sodium hydroxide pellets in 1000 mL of DI water in a volumetric flask. This reagent is used for both the Cyanide and Sulfide tests.

- Life of Reagent: 1 year
- Storage Requirements: none

5.8 Potassium bi-iodate, 0.0021 M

This reagent is purchased from a reputable vendor. If the reagent must be made in the lab, use an analytical balance capable of measuring 0.1 mg, quantitatively transfer 0.8124 g potassium bi-iodate to a 1.0 L volumetric flask using DI water.

- Life of Reagent: 1 year
- Storage Requirements: none

5.9 Sodium Hydroxide, 6 N

Dissolve 240 g of sodium hydroxide into 1.0 liter of DI water.

- Life of Reagent: 1 year
- Storage Requirements: none

5.10 0.1 N Sulfuric Acid

Dilute 2.8 mL concentrated H_2SO_4 to 1.0 L to make the 0.1 N H_2SO_4. . This reagent is used for reactive sulfide.

- Life of Reagent: 1 year
- Storage Requirements: none

5.11 0.5 M Zinc Acetate

Dissolve 110 g Zinc acetate dihydrate in 200 mL of reagent water. Add 1 mL of concentrated HCl to prevent precipitation of zinc hydroxide. Dilute to 1 liter.

- Life of Reagent: 1 year
- Storage Requirements: none

5.12 20 % Sulfuric Acid

To a 1.0 L volumetric flask containing ~600 mL DI water, slowly add 200 mL of concentrated sulfuric acid. . Mix thoroughly. . When cool, dilute to volume with DI water.

- Life of Reagent: 1 year
- Storage Requirements: none

5.13 Aluminum Chloride solution

Dissolve the contents of a previously unopened 100-gram bottle of $AlCl_3 \cdot 6H_2O$ in 100 mL of DI water.

Life of Reagent: 1 year
Storage Requirements: none

Alternatively, this reagent can be purchased in 125 mL volumes from Ricca Chemical Company, Ricca Catalog # 510-4, through VWR. . The shelf life provided on container is ~2 years.

5.14 Sulfite Test Strips

Sulfite Test Strips - Quantofix 10 – 1000 mg/L SO_3^{2-} (Colorimetric) 100 Qty

Life of Reagent: Follow manufacturers expiration date
Storage Requirements: Dry Place; 2°C to 8°C

This item may be purchased from Fisher Scientific, Catalog # M110013001.

6.0 CALIBRATION (NON-DAILY)

Not Applicable.

7.0 PROCEDURE

7.1 Quality Control Checks

The following Quality Control standards are inherent in each analytical batch.

Quality Controls	Frequency	Control Limit
Iodine Standardization	Prior to Analysis	NA
Method Blank (MB)	1 in 20 samples	< Reporting Limit ; <1/2 RL (per QAPP)
Laboratory Control Sample (LCS) [1]	1 in 20 samples	85-115%; ≤ 20 RPD (Water) 80-120%; ≤ 20 RPD (Soils)
Matrix Spike/Matrix Spike Duplicate (MS/MSD) [2,3]	1 in 20 samples	75 - 125%; ≤ 20 RPD

[1] LCS Duplicate (LCSD) is done only when insufficient sample is available for the MS/MSD or when requested by the client/project/contract.
[2] The sample selection for MS/MSD is rotated among client samples so that various matrix problems may be noted and/or addressed.
[3] Matrix Duplicate (DU) is done only when requested by the client/project/contract. . An MS and MSD are done routinely.

7.2 Sample Preservation and Storage

Holding time, preservation techniques and sample container may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client request. . Listed below are the holding times and the references, which include the container and

preservation requirements for compliance with the Clean Water Act (CWA). . The text in 9030B is vague concerning the holding time for non-aqueous matrices, and the regulations were written for waters. . Eurofins Test America Chicago limits the holding time of extracts to 7 days.

Regulation	Holding Time	Preservative (Water)	Reference
CWA	7 days	≤ 6°C, Zn acetate, NaOH to pH >9; Zero Headspace	40 CFR Part 136.3

Aqueous samples must be collected with minimal agitation and with zero headspace in the bottles, when possible, to prevent loss of sulfide.

7.3 Sample Preparation

7.3.1 Sample Size

Matrix	Sample Size
Waters	250 mL
Soils / Wastes	10 grams

7.3.2 Sample Preparation - General

7.3.2.1 If the sample contains solid objects that cannot be reduced in size by tumbling, the solids must be broken manually. . The solids must be reduced to a size that will be suspended by the bubbling action of the Westco system.

7.3.2.2 Non-porous harder objects that are representative of the sample matrix, for example stones or pieces of metal, may be weighed and discarded. . This is done by removing rocks, etc., from the sample after the initial weighing.

7.3.3 Sample Preparation - Waters for Total Sulfide (Std. Mds., 20th Ed., Method 4500S^{-2}B and C

7.3.3.1 Remove the sample container lid, and with a glass rod, remove a drop of sample and place it onto a strip of broad-ranged pH paper. . The pH should be >9. . If a water sample is received unpreserved, add 1.5 mL of 0.5 M zinc acetate solution to a 500 mL bottle. . With minimal agitation, fill with sample. Add 0.50 mL (10 drops) 6 N sodium hydroxide solution. Alternatively, add one zinc acetate-sodium hydroxide preservative ampule to 1 L of sample. . Mix well by rotating the bottle back and forth about a transverse axis. . Let the precipitate settle for 30 minutes. The treated sample is relatively stable. . However, if much iron is present, oxidation may occur.

7.3.3.2 If a sample is known to contain interferences, the preserved sample may be de-watered by filtering a known volume through a glass fiber filter (Reference Method 4500S^{-2}C). . The zinc sulfide precipitate is captured on the filter, and the filtrate that contains interferences is discarded. . This procedure may also be used to concentrate larger volumes of sample to achieve a lower reporting limit. . Specifically see Section 7.6.2 for de-watered samples.

7.3.3.4. If ***dissolved*** sulfide is required, add 1.0 mL of 6 N NaOH to a 500 mL bottle. . Fill the bottle with unpreserved sample and add 1.0 mL of aluminum chloride reagent. . Close the bottle, eliminating air entrapment. Mix very well by gentle inversion for one minute to flocculate the contents. . Allow the flocculent to settle until the sample is reasonably clear, but do not wait longer

than necessary. Draw off 250 mL of the cleared supernate for analysis, using a class A graduated cylinder. . Preserve as in Section 7.3.3.1

Proceed to Section 7.4.

7.3.4 Sample Preparation - Solid Samples for Total Sulfide (SW-846 Method 9030B)

7.3.4.1 Weigh 10 grams to the nearest 0.1 gram of well-mixed sample, into a tared Westco boiling tube, or weigh the sample portion onto a tared piece of parafilm or weigh boat and transfer into a Westco tube. . The sample weight can be recorded directly in the ADII prep batch electronically.

7.3.4.2 Add 50 mL of DI water to each sample, the MS and MSD, and to separate tubes for the MB and LCS.

7.3.4.3 Add 10.0 mL of well-mixed stock sulfide to the LCS, MS, and MSD. . This is best accomplished by setting the stock solution on a stir plate, adding a stir bar, and mixing at a steady rate. . While mixing, withdraw the 10.0 mL using a 10.0-mL volumetric pipet. The sulfide is contained in the suspended precipitate of the standard.

7.3.4.4 Place the inlet adapter tube into the prepared boiling tubes and place into the block digester.

7.3.4.5 Close the stopcock of the Westco addition funnels and add 50 mL of 20% sulfuric acid to the funnel. . This volume of acid will neutralize and pH adjust 10 g NaOH, thereby ensuring that any 10-gram sample will be adequately acidified. . Cap the addition funnels and set them on top of the inlet tubes.

7.3.4.6 Add 50 mL of 0.25 N NaOH and 5 mL of 0.5 M zinc acetate to 2 Westco scrubbing vessels for each sample/standard.

7.3.4.7 Connect all the glassware and gas tubing, ensuring tight fits.

7.3.4.8 Open the N_2 gas regulator slightly, and adjust the system so that the gas is bubbling through all the glassware. . The gas flow not only sweeps the sulfide gas into the scrubbers, it also “stirs” the samples during the extraction.

7.3.4.9 Allow to purge for approximately 10 minutes to remove the oxygen from the system. . Make sure that each tube is bubbling. . Some samples tend to block the inlet tube, and may require lifting the tube from the bottom of the sample while the gas is flowing to release a plug, or increasing the gas flow, or both.

7.3.4.10 At this point in the process, solid samples originating in the state of Wisconsin will be checked for the presence of sulfite using a Sulfite Test Strip that is sensitive to the presence of sulfite at 10 mg/L. The Lot # of the Sulfite Test Strip will be recorded in the AD Batch. If sulfite is present in the sample solution at a concentration greater than 10 mg/L an NCM must be written stating that there is a potential for bias associated with the sample result due to the presence of sulfite in the solid sample. Note: The formaldehyde recommended in the 9030B method to reduce the interference is not used by the laboratory due to safety concerns.

7.3.4.11 Turn on the heating block, after programming it for sulfide. . (The block ramps at a rate of 8 °C per minute to 70 °C, and holds that temperature for 1.5 hrs.)

7.3.4.12 Open the addition funnel stopcocks gently, watching for excess reactivity. . When all the acid is dispensed, re-close the stopcocks and allow the reaction to occur for 90 minutes, checking the gas flow frequently.

7.3.4.13 After 90 minutes, turn off the gas and disassemble the apparatus. . The contents of both scrubbers are combined and titrated. .

7.3.4.14 The pH of the spent sample after the 90 minute reaction period must be taken using pH paper range 0.5 – 5.0 S.U. and recorded in the sample preparation AD Batch. The Lot # of the pH paper used will also be recorded in the AD Batch. If the pH of the spent sample solution is not $\leq$ 1 the sample must be re-distilled using additional sulfuric acid.

7.3.4.15 If the pH of the spent solution is $\leq$ 1 then proceed to Step 7.6.

7.3.5 Sample Preparation - Waste Samples for Reactive Sulfide SW-846, Section 7.3.4.2

7.3.5.1 Weigh 10 grams of sample to the nearest 0.1 gram, into a tared Westco boiling tube, or weigh the sample portion onto a tared piece of parafilm or weigh boat and transfer into a Westco tube. . Record the sample weight in the weigh log.

7.3.5.2 Add 100 mL of DI water to each sample, the MS and MSD, and to separate tubes for the MB and LCS.

7.3.5.3 Add 10.0 mL of well-mixed stock sulfide to the LCS, MS, and MSD. This is best accomplished by setting the stock solution on a stir plate, adding a stir bar, and mixing at a steady rate. . While mixing, withdraw the 10.0 mL using a 10.0-mL volumetric pipet. The sulfide is contained in the suspended precipitate of the standard.

7.3.5.4 Place the inlet adapter tube into the prepared boiling tubes and place into the block digester.

7.3.5.5 Close the stopcock of the Westco addition funnels and add 11 mL of 0.1 N sulfuric acid to the funnel. This amount added to the 100 mL in the boiling tube will be equivalent to 0.01N sulfuric as required by SW 846. . Set the addition funnels on top of the inlet adapters.

7.3.5.6 Add 50 mL of 0.25 N NaOH and 5 mL of 0.5 M zinc acetate to one Westco scrubbing vessels for each sample/standard. . Assemble all the Westco glassware and gas tubes.

7.3.5.7 Slowly turn on the N_2 gas with the regulator set on the lowest mark. . Check for consistent bubbling throughout the system, and allow the system to purge for approximately 10 minutes. . (See 7.3.4.10)

7.3.5.8 Open the stopcock to allow the acid in the addition funnel to boiling tube with sample. . Allow the reaction to proceed for 30 minutes, then disassemble the apparatus. . The sulfide trapped in the scrubber is now ready for analysis.

7.3.5.9 Proceed to Section 7.6.

7.3.6 Sample Preparation - Water Samples for Reactive Sulfide SW-846, Section 7.3.4.2

Same as the waste procedure (Section 7.3.5) except the sample size is 100 mL rather than 10 grams. . Note: The reactive sulfide procedure is not performed for waters samples, the total sulfide analysis is performed and reported as reactive sulfide to the client. An NCM is written stating that the total sulfide analysis was performed for the water sample.

7.4 Calibration and QC Preparation

7.4.1 Standardization of Iodine

NOTE: The iodine is standardized daily prior to each use.

7.4.1.1 Using a volumetric pipette, add 5.0 mL of iodine reagent to each of three 125 mL Erlenmeyer flasks and dilute to 100 mL with DI water.

7.4.1.2 Add approx. 5 mL 6 N hydrochloric acid (Rgt. 5.3) to each.

7.4.1.3 Back titrate each sample with Std. Sodium Thiosulfate until the solution becomes pale yellow.

7.4.1.4 Add ~0.5 mL of the 2% Starch Solution or starch powder (the color of the sample solution should turn a dark blue - black; if not, the solution has been titrated too far).

7.4.1.5 Continue titrating each of the three until the solution becomes clear. . Record the titrant volumes.

7.4.1.6 Use the average mL of titrant in calculating the normality of iodine.

7.4.2 Method Blank (MB) (Water)

Use 250 mL DI Water.

7.4.3 Laboratory Control Sample (LCS) (Water)

Using a 5.0 mL volumetric pipette, add 5.0 mL of well-mixed Stock Sulfide Solution to 250 mL of DI water measured into a 250 mL volumetric flask. . This is best accomplished by withdrawing the 5.0 mL while the stock is mixing on a stir plate.

LCS concentration: ~4.0 mg/L. . The “true value” is determined at the time of preparation of the ~200 mg/L stock solution. .

7.4.4 Matrix Spike / Matrix Spike Duplicate (MS/MSD) (Water)

Using a 5.0 mL volumetric pipet, add 5.0 mL of well-mixed Stock Sulfide Solution to 250 mL of sample in a 300-mL flask. . Note that the sulfide is contained in the suspended precipitate of the standard. . It is best to withdraw the stock solution while the stock is mixing on a stir plate.

Concentration: ~4.0 mg/L (See note in 7.4.3) for a 250 mL sample. .

7.4.5 Soil / Waste Method Blank

For Reactive Sulfide use 100 mL DI water and for Total Sulfide use 50 mL DI water in the Westco sample tubes and treat as a sample.

7.4.6 Soil / Waste Laboratory Control Sample (Total or Reactive)

Using a 10.0 mL volumetric pipette, add 10.0 mL of well-mixed Stock Sulfide Solution to the Westco sample tube. For Reactive Sulfide use 100 mL DI water and for Total Sulfide use 50 mL DI water. . Note that the sulfide is contained in the suspended precipitate of the standard.

Concentration: ~200 mg/Kg, assuming 10 grams sample. . See note in 7.4.3. .

7.4.7 Soil / Waste Matrix Spike / Matrix Spike Duplicate (Total or Reactive)

Using a 10.0 mL volumetric pipette, add 10.0 mL of well-mixed Stock Sulfide Solution to the Westco tube containing ~10 grams of sample. . Note that the sulfide is contained in the suspended precipitate of the standard.

Concentration: ~200 mg/kg.

7.5 Preventive Maintenance

- Wash and rinse all tubing daily of any waste particles left inside. . Always shut off the gas valve after daily use.
- Rinse the burette with DI water and titrant prior to each use to prevent contamination. . Rinse with DI water after each use.
- Periodically rinse the tubing with 10% nitric acid, followed by DI water rinsing.
- Replace tubing when old or cracked.

7.6 Sample Analysis

7.6.1 SW846 9030B or Reactive Sulfide Preparations:

7.6.1.1 Pipet 5.0 mL of standardized 0.025 N iodine and approximately 20 mL of DI water to a ≥ 300 mL Erlenmeyer flask, using the water to rinse all traces of iodine into the bottom of the flask.

7.6.1.2 Add 6 N HCl in the following amounts:

Total (2 scrubbers)	Reactive (only 1 scrubber)
9 mL HCl	6 mL HCl

7.6.1.3 Keeping the pipet tip below the surface of the iodine solution, pipet the contents of the gas scrubbers into the flasks. . A funnel with tubing attached may be used to dispense the sample below the iodine solution level in the titration flask. . If the solution does not retain the yellow color, add more 6 N HCl, then if necessary, additional 5.0 mL increments of 0.025 N iodine until the color remains, recording the total amount of iodine used.

NOTE: When adding additional iodine, the sample may become turbid and the yellow color change may be difficult to perceive. . At this point, add ~0.5 mL of the 2% Starch Indicator (Rgt. 5.5) for a distinct blue color change (this occurs in samples with high sulfide content).

7.6.1.4. Continue titrating until the first complete disappearance of the blue color. . Blue tinge will come back after sitting. . No additional titration is required.

7.6.2 For Dewatered Sample Preparations

7.6.2.1 Place the filter containing the zinc sulfide precipitate into a suitable flask. . Add 5.0 mL of standardized ~0.025 N iodine and enough DI water to cover the filter. . Then add 6 mL of 6 N HCl and re-suspended precipitate by gently swirling. . If the solution does not retain the yellow color, add additional 5.0 mL increments of 0.025 N iodine until the color remains, recording the total amount of iodine used.

NOTE: When adding additional iodine, the sample may become turbid and the yellow color change may be difficult to perceive. . At this point, add ~0.5 mL of the 2% Starch Indicator (Rgt. 5.5) for a distinct blue color change (this occurs in samples with high sulfide content).

7.6.2.2 Back titrate with Std. Sodium Thiosulfate (Rgt. 5.4) until the solution turns a straw color, and then add ~1.0 mL of Starch Indicator (Rgt. 5.5). . The color should be blue - black (if the sample remains straw color or colorless, you have titrated too far).

7.6.2.3 Continue titrating until the first complete disappearance of the blue color. . Record the titrant volume used. . The blue color may come back after sitting. . No additional titration is necessary.

7.6.3 For preserved water samples.

7.6.3.1 Pipet 5.0 mL of standardized 0.025 N iodine and approximately 20 mL of DI water to a ≥ 300 mL Erlenmeyer flask, using the water to rinse all traces of iodine into the bottom of the flask. . Add 3 mL of 6 N HCl.

7.6.3.2 Gently invert and swirl the sample to suspend the zinc sulfide precipitate, then pour the appropriate volume (usually 250 mL) through the extension funnel into the flask, keeping the tip below the iodine level.

7.6.3.3 Back titrate with Std. Sodium Thiosulfate (Rgt. 5.4) until the solution turns a straw color, then add enough Starch Indicator (Rgt. 5.5). . The color should be blue - black (if the sample remains straw color or colorless, you have titrated too far).

7.6.3.4 Continue titrating until the first complete disappearance of the blue color. . Record the titrant volume used. . The blue may return upon sitting. . No additional titration is necessary.

7.7 Documentation

7.7.1 Analysis Logbook

The analysis of samples and standards is documented within the instrument run log. . The runlog must be completed for each day's analysis. . An example of an analysis log page appears in Attachment 1. .

7.7.2 Traceability of Standards

Upon receipt or preparation, each chemical salt, solvent, acid, standard, or other reagent is entered into the laboratory's TALs LIMS and is issued a unique ID# based upon the type and sequential order in which the item was received. . Further information entered into the database includes the manufacturer, lot # (if applicable), the date received or prepared, the expiration date, volume/weight received; concentration (if applicable); preparation details (if applicable), initials of the recording analyst, and the description of the item. . Once the record is created, a unique label is printed and affixed to the appropriate standard/reagent container. .

7.7.3 Data Review

Analytical data goes through a 200% review cycle. As results are generated, analysts review their work to ensure that the results generated meet QC requirements and relevant EPA methodologies. The analyst transfers the data into TALs in the Analyst Desktop module. Where non-compliance is observed, the analyst creates Non-Conformance Memos (NCMs) in TALs. Flags and data qualifiers can be method, project, program or QAPP specific. The analyst documents the initial review and sets the batch status in LIMs to 1st level review. The second level or peer review of the data is conducted by another individual who has been trained on the review process. This secondary review is documented in the same AD batch, making any necessary corrections to the data or additions to the NCMs as necessary. The batch is then set to 2nd level review. Any Spectra and all manual integrations are reviewed. The raw data, including instrument print-outs, and manual entries, and electronic files are retained for easy retrieval in accordance with the laboratory's record and retention policy outlined in the SOP, *UP-QA-QAM, Section 16*.

Examples of items included in the above reviews are as follows:

- QC data are outside the specified control limits for accuracy and precision
- Unusual detection limit changes are observed
- Samples having unusually high results
- Samples exceeding a known regulatory limit
- Raw data indicating some type of contamination or poor technique
- Transcription errors

7.7.4 Reporting Results

Without rounding, enter the raw data into the ADII module of TALS. . Review the entries. . The data book must be compared with the TALs batch on screen.

8.0 QUALITY CONTROL

8.1 QC Summary

8.1.1 At least one MB, LCS and MS/MSD pair will be included in each laboratory lot of 20 samples. If insufficient sample is available to perform an MS/MSD, and LCSD will be performed.

8.1.2 The MBs will be examined to determine if contamination is being introduced in the laboratory. .

8.1.3 Accuracy will be measured by the percent recovery of the LCS. The recovery must be within the acceptance criteria in order to be considered acceptable. Additionally, the percent recovery will be plotted on control charts to monitor method accuracy.

8.1.4 Precision will be measured by the reproducibility of the MS/MSD or the LCS/LCSD if an MS/MSD is not performed.

8.2 Corrective Actions

When an out of control situation occurs, the analysts must use their best analytical judgment and available resources to determine the corrective action to be taken. The out of control situation may be caused by more than one variable. The analyst should seek the assistance of his/her immediate supervisor, QA personnel, or other experienced staff if he/she is uncertain of the cause of the out of control situation. The test must not be resumed until the source of the problem and an in-control status is attained. . All samples associated with the out of control situation should be reanalyzed. Out of control data must never be released without approval of the supervisor, Project Manager, QA personnel or the Laboratory Director.

Listed below are steps that MUST be taken when an out of control situation occurs:

- demonstrate that all the problems creating the out of control situation were addressed;
- document the problem and the action which was taken to correct the problem in the logbook and in a non-conformance memo (NCM);
- document in the logbook and in an NCM that the system has been brought back within control limits; and
- receive approval (signature) of the supervisor, Project Manager, QA personnel, or the laboratory director prior to the release of any analytical data associated with the problem;

Suggested Actions to specific out of control situations:

8.2.1 Laboratory Control Sample (LCS)

If the LCS is Low:

- when possible, as in a water set, re-prep and reanalyze LCS to verify that an out of control situation exists;
- determine the source of error within the preparation procedure and correct the problem. Soil sets will need to be repeated.

If the LCS is High:

- re-prep and reanalyze LCS to verify that an out of control situation exists;
- determine the source of contamination or error within the preparation procedure, correct the problem and repeat the sample set. (Sources of contamination could be the reagents, the LCS stock solution, or the preparation area.) All samples that are less than the reporting limit may be reported, even though the LCS is high, but the situation must be documented and an NCM must be written.

8.2.2 Method Blank (MB)

- when possible, re-prep and reanalyze MB to verify contamination;
- determine the source of contamination and correct the problem;
- all samples above the RL (>1/2 RL, or LOD per QAPP) whose concentration is <10 times the MB level must be reprocessed and reanalyzed; any sample which is >10 times the MB level

need not be reanalyzed. . However, note the out-of-control MB in the logbook and an NCM must be written. .

8.2.3 Matrix Duplicate (DU)

- the sample must be reprocessed and reanalyzed unless the sample concentration is <5 times the MDL, then the ± MDL rule applies;
- if the reanalysis is within the control limits, the second value is reported;
- if the reanalysis is still outside of the control limits, note the situation in the logbook and on an NCM.

8.2.4 Matrix Spike / Matrix Spike Duplicate (MS / MSD)

- If a single spike is performed and it is outside the acceptance limits, it must be repeated to verify the matrix effect. Generally, an MS and MSD are performed together in the same batch as the original sample analysis, but must be related properly in any case.
- Report all spikes, whether or not they are in control.
- Note out-of-control spikes in the logbook and write an NCM.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 Normality of Iodine

$$N = \frac{A\ X\ B}{C}$$

Where:
A = mL of $Na_2S_2O_3$ titrated (average of 3 titrations)
B = Normality of $Na_2S_2O_3$
C = mL of Iodine

9.2 Solid Samples

$$\frac{\text{mg}}{\text{Kg}}(\text{wet weight}) = \frac{[(\text{A X B}) - (\text{C X D})]\ \text{X}\ 16{,}000}{\text{Sample weight (g)}}$$

$$\frac{\text{mg}}{\text{Kg}}(\text{dry weight}) = \frac{\frac{\text{mg}}{\text{Kg}}(\text{wet weight})}{\%\ \text{solids (as a decmial)}}$$

Where:
A = normality of iodine
B = mL of iodine used
C = normality of sodium thiosulfate
D = mL of sodium thiosulfate

The dry weight correction is made automatically in AD in LIMS, once the % solids result is at 2nd Level Review status.

9.3 Water Samples

$$\frac{mg}{L} = \frac{[(A \times B) - (C \times D)] \times 16{,}000}{\text{Sample Volume (mL)}}$$

Where:
A = normality of iodine
B = mL of iodine used
C = normality of sodium thiosulfate
D = mL of sodium thiosulfate

9.4 Accuracy

9.4.1 LCS % Recovery

$$\frac{\text{observed concentration}}{\text{actual conceentration}} \times 100$$

9.4.2 Matrix Spike % Recovery

$$\frac{(\text{spiked sample conc.}) - (\text{unspike sample conc.})}{\text{spiked concentation}} \times 100$$

9.5 Precision

9.5.1 MS/MSD or MD Relative Percent Difference (RPD)

$$RPD = \frac{|\text{original sample value} - \text{duplicate sample value}|}{\frac{(\text{orginal sample value} + \text{duplicate sampe value})}{2}} \times 100$$

10.0 POLLUTION CONTROL

It is Eurofins policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

10.1 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to UP-WM-001.

The following waste streams are produced when this method is carried out.

- Acidic waste generated by the addition of HCl to the samples is disposed of in the corrosive waste stream. . The waste does contain zinc, however, zinc is not a toxic metal.

11.0 METHOD PERFORMANCE CRITERIA

Refer to Sections 1, 6, 7 and 8.

12.0 REFERENCES

Refer to Section 1.

13.0 ATTACHMENTS

Attachment 1: Example: Analysis Logbook

14.0 REVISION HISTORY

- Revision 30 updated on 05/22/23
- Annual Review
- Section 1.0 corrected numbering error.
- Section 1.0 added 4500-S^2-F 23rd ED
- Section 1.1.1 updated corporate SOP
- Section 1.1.3 removed chart
- Section 8.2.1 and 8.2.2 clarified the reanalysis of batch QC
- Throughout removed reference to data review checklist and corresponding attachment

Attachment 1.

Example: Analysis Logbook

Eurofins Chicago
Sulfide / Reactive Sulfide

Page #: _____

Method:
SM4500S2-F-00 _____ SW-846 9034 _____
SW-846 9030B/9034 _____ SW-846 7.3.4.2/9034 _____

NCM #: _____
Analytical Batch #: _____
Prep Batch #: _____

Normality of I_2:

Trial 1 = _____ mLs
Trial 2 = _____ mLs
Trial 3 = _____ mLs
Avg. = _____ mLs

Titration Dispener ID: _____

$$N\ I_2 = \frac{(\text{Avg. mLs} \times N\ Na_2S_2O_3) / 5}{}$$

N of $Na_2S_2O_3$ = _____
N Check: Date:_____ Book No.:_____ Page No.:_____

Result (mg/L or mg/kg) = (mLs I_2)(N I_2) - (mLs $Na_2S_2O_3$) (N $Na_2S_2O_3$) x 16,000 / Sample Size (mLs or grams)

Sample #	Sample Size	mLs I_2	mLs $Na_2S_2O_3$	% Rec. (RPD)	Comments

Comments: _____

Standards Traceability

Stock Soln. I ID # (LCS/MS):_____ Standardization: Book_____Page_____
Note: Working standards are prepared daily from noted Stock Solution.
Spiking Levels (mg/L): LCS:_____ MS (Water):_____ MS (Soil):_____

Preparation (Circle): a. Filtered b. Bubbled c. Bubbled with Heat

Prep Analyst:_____ Date/Time: _____
Analyst:_____ Date/Time: _____
Reviewer:_____ Date: _____

CHI-22-0451-05/14

TITLE: WET CHEMISTRY
Total and Volatile Dissolved Solids

Approvals (Signature/Date):

Paul Kolarczyk 4-18-24
Paul Kolarczyk Date
Supervisor, Wet Chemistry

Chris Hoham 4/18/24
Chris Hoham Date
Env. Health & Safety Coor.

Nicole Berg 4/18/24
Nicole Berg Date
Quality Assurance Manager

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1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) is used to determine the concentration of total dissolved and volatile dissolved solids (TDS / VDS) in drinking, surface, and ground waters, domestic and industrial wastes. This SOP was written using the following as primary references:

- Total Dissolved Solids (TDS): Standard Methods 2540C-97, 2540C-11, 2540C-15, 2540C-23rd Ed.
- Volatile Dissolved Solids (VDS): Standard Methods 2540E-97, 2540E-11 & EPA 160.4 (91).

TDS is a secondary Drinking Water Contaminant with a limit of 500 mg/L (non-enforceable). High dissolved solids in drinking water are an indication that unpleasant odors and tastes may be present and that some consumers may experience digestive problems if not accustomed to the water source.

On occasion, clients request slight modifications to this SOP for non-drinking water samples. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP) and authorized via laboratory signature approval; and amended to the data packages case narrative. Note: There are no method modifications allowed for Drinking Water samples without prior written approval from the US EPA.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants" with additional details are provided in the Eurofins Corporate SOP, *NDSC-QA-SOP42091, Detection Limits* and the Eurofins Chicago SOP, *UP-QA-017, Method Detection Limit Studies.* MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; the MDL will be performed and verified on an annual basis verifying the Lower Limit of Quantitation (LLOQ) for the method

1.1.2 Demonstration of Capability

Before the laboratory may institute a new method and begin reporting results, the laboratory shall confirm that it can properly operate the method. A demonstration of capability is performed whenever there is a change in instrument type, method or personnel. An Initial Demonstration of Capability (IDOC) must be thoroughly documented and approved by the Department Manager/Supervisor and QA Manager prior to independently analyzing client samples. All associated documentation must be retained in the QA Department and in the Analyst Training files. For additional details on the demonstration of capability procedures followed, refer to the laboratory SOP, *UP-QA-QAM, Quality Assurance Manual, Sections 19.4.2 and 19.4.3.*

1.1.3 Reporting Limits (LLOQ)

Reporting Limits (LLOQ) are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. The laboratory maintains reporting limits that are higher than the MDL. Wherever possible, reporting is limited to values ~3-5x the respective MDL to ensure confidence in the value reported.

Matrix	Reporting Limit
Waters	10 mg/L

1.1.4 Definitions

Refer to Section 3.0 of the Laboratory's Quality Assurance Manual (UP-QA_QAM).

1.2 Summary of Methods

Drinking water which contains high TDS is likely to contain excessive amounts of substances which are aesthetically objectionable to the consumer. High TDS frequently results in water with a general poor taste. Solids in excess of 1,000 mg/L tend to have deleterious economic impacts on water distribution systems and household plumbing.

The term TDS is often interchanged with total filterable residue. These terms reflect the sum concentration of the individual dissolved ions and molecules. The dissolved solids test is a screening procedure since an analysis of the individual ions is necessary to properly describe the water. A well mixed sample is filtered through a standard glass fiber filter with a pore size of approximately 1.5 to 2.0 µm. The filtrate is evaporated at 104 ± 2°C and dried to constant weight at 180 ± 2 °C.

Essentially the same procedure is followed for the term "residue on evaporation" or "ROE" used by the State of Illinois, except that the samples are filtered in the field through 0.45 µm membrane filters and are not filtered in the laboratory.

VDS results are obtained by subjecting the residue from the TDS to ignition in a muffle furnace at 550 ˚C.

2.0 INTERFERENCES

- Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.
- Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying to insure that all the bicarbonate is converted to carbonate.
- Too much residue in the evaporation dish will crust over and entrap water that may not be driven off during drying. Total residue should be limited to 200 mg.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual, Lab Specific Addendum to the CSM, and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coat and closed-toe, nonabsorbent shoes are a minimum.

3.1 Specific Safety Concerns or Requirements

Care should be taken when removing heated crucibles from the oven. Heat resistant gloves or tongs should be used when removing crucibles or racks.

3.2 Primary Materials Used

There are no materials used in this method that have a significant or serious hazard rating. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

4.0 EQUIPMENT AND SUPPLIES

- Balance accurate to 4 decimal places
- Desiccator
- Buchner funnel
- Glass fiber filters
- Porcelain or glass evaporating dishes
- Steam bath or hot plate (optional)
- Ovens, 102-106ºC, 178-182ºC
- Static Master
- Vacuum pump
- Sidearm flask
- 10 ml wide-bore disposable pipette
- Class A graduated cylinders, various sizes
- Stable Weigh pre-weighed vessels
- Environmental Express TDS Hot Block
- Forceps

5.0 REAGENTS AND STANDARDS

All standards and reagents are prepared with Type II Deionized (DI) Water, unless otherwise stated, in Class A volumetric flasks.

5.1 Stock Sodium Chloride Solution; 25,000 mg/L

Dry ~35 grams of sodium chloride (NaCl) in an oven at 105ºC for one hour and cool in a desiccator to room temperature. On a balance capable of reading 0.1 mg, weigh out 25.000 g of this dried reagent. Quantitatively transfer to a 1.0 L volumetric flask and dilute to volume with DI

water. Add a clean stir bar and place on stir plate until all the NaCl is dissolved. Remove the stir bar and transfer the solution to a clean, rinsed and properly labeled reagent bottle.

- Life of Reagent: 1 - year
- Storage Requirements: Keep capped.

5.2 Quality Control Samples

Standard	Preparation
Method Blank (MB)	50 mL DI water
Lab Control Sample (LCS) (250 mg/L)	50 mL DI water spiked with 500 µLs of Stock NaCl Solution.
Matrix Duplicate (DU)	Volume of sample identical to original sample.
Matrix Spike (MS) (250 mg/L)	50 mL sample spiked with 500 µLs Stock NaCl Solution. (If less or more sample volume is used, spike at the ratio of 500 µLs of Stock Solution to 50 mL of sample.)

Note: Standard Methods does not require a matrix spike, but that is part of Eurofins Chicago's routine QC program. See below.

6.0 CALIBRATION (NON-DAILY)

Not Applicable.

7.0 PROCEDURE

7.1 Quality Control Checks

Quality Controls	Frequency	Control Limit [1]
MB	1 in 20 samples	< Reporting Limit < MDL (Drinking Water)
Laboratory Control Standard (LCS)[2]	1 in 20 samples	80 – 120%
Matrix Spike (MS)[3]	1 in 20 samples	75 – 125%
Matrix Duplicate (DU)[3]	1 in 10 samples	≤ 5 RPD

[1] Refer to Section 8.0 for additional details.
[2] LCS Duplicate (LCSD) is done only when insufficient sample is available for matrix QC or when requested by the client/project/contract.
[3] Sample selection for matrix QC is rotated among client samples so that various matrix problems may be noted and/or addressed.

7.2 Sample Preservation and Storage

Holding time, preservation techniques and sample container may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client request. Listed below are the holding times and the references which include container and preservation requirements for compliance with the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA).

Regulation	Holding Time	Preservation	Reference
CWA	*7 days	Cool 4 ± 2°C	CFR 40 pt. 136.3
SDWA	*7 days	Cool 4 ± 2°C	EPA 600/4-79-020

* Eurofins Chicago interprets holding times that are given in days to mean that analysis completed any time within the final day of the holding time is acceptable. There are some clients that interpret the holding time to mean that the analysis must be complete on the final day by the time of day that the sample was collected, in other words in this case, 168 hours after collection.

7.3 Sample Preparation

7.3.1 Sample Size.....50 mL, or less if the residue is known to be very high.

7.3.2 Preparation of Glass Fiber Filter Disc

Whatman™ 24mm934-AH™ filters (or equivalent) are used and they must be handled with tongs or forceps. Place the disc, wrinkled side up, in the Buchner funnel or other filter holding device. With the vacuum applied, wash the disc with 3-successive aliquots of water (20 mL each). Remove all traces of water by continuing to apply the vacuum after the water has passed through. Discard all washings.

7.3.3 Preparation of Evaporating Dishes

- When crucibles are used for TDS, heat the clean dish to 180 ± 2°C for at least an hour. Cool in a desiccator and store until needed. Weigh and record immediately before use.
- When the Stable Weigh vessels (bags) are used for TDS, the use of a static reducing device prior to weighing may help eliminate noise caused by static.
- If VDS is to be done, use a ceramic evaporating dish that has been muffled at a temperature of 550 ± 50°C for at least an hour, cooled, and kept in a desiccator for at least an hour. Weigh and record immediately before use.

7.4 Calibration / Standardization

- Laboratory balances will be calibrated and serviced annually by a certified vendor in balance calibration and repair. In addition, the balance will be checked daily with Class S weights or a weight set calibrated against a Class S set. A record of calibrations and daily checks will be kept in the Balance Calibration module in TALS.
- Daily oven temperatures will be recorded in the AD batch along with the thermometer ID. Additionally, the corrected temperature of the appropriate ovens will be recorded in the TDS book when samples are put in and taken out. The oven thermometers are calibrated annually against an NIST certified thermometer in the range of interest.

7.5 Preventive Maintenance

- Clean the balance after each use.
- Verify that the daily oven calibration check has been performed and is in control (178-182°C) prior to use. The temperature is to be recorded when the oven is stable. Corrective action must be performed and recorded in the Daily Oven Temperature Control Log (CHI-22-12-082) when needed.
  Note: The oven temperature may be unstable while samples are inside evaporating.
- Desiccant is inspected daily by the analyst. If the desiccant requires re-drying, place in a glass beaker and place it in the oven overnight. Desiccant changes from a blue hue to a pink hue when drying is necessary. Alternatively, if the desiccator is equipped with a humidity-indicating gauge, that may be used as the indication for the analyst to re-dry the desiccant.
- Change the oil in the vacuum pump monthly or as needed.

7.6 Sample Analysis

7.6.1 Assemble the filtering apparatus and start the vacuum. Shake the sample vigorously and quantitatively transfer a measured portion to the filter using a graduated cylinder. Work rapidly to prevent settling of the solids in the sample bottle. If less than 20 mL will be analyzed, Standard Methods suggests that the sample be stirred on a stir plate while the sample aliquot is removed by wide-bore pipet from a point midway in the container, halfway between the wall of the container and the vortex. *Note: It is important to retain the integrity of the sample that remains in the container for other tests that may follow.*

Note: The wide-bore pipet is not to be used for samples that require compliance with the BP LaMP or TransCanada programs, only Class A glassware is acceptable for use.

7.6.2 Filter the sample through the glass fiber filter, rinse the graduate and filtration apparatus with 3 small but thorough aliquots of DI water and continue to apply the vacuum after filtration is complete to remove as much water as possible. Max filtration time should not exceed 10 minutes.

7.6.3 Quantitatively transfer the entire filtrate to a weighed evaporating dish or vessel, rinsing as appropriate, at least three times with a small stream of DI water. It may be helpful to secure an Eppendorf tip to the outlet of a plastic squeeze bottle to obtain a small enough water stream.

7.6.4 Let the sample evaporate until visibly dry, to accomplish this, the evaporating dishes are placed into a 103-105° C oven or hot block until dry for approximately 11 hours.

7.6.4.1 Transfer the dish to the 180 ± 2°C oven for at least 1-hour. Cool in a desiccator for a minimum of 30 minutes and weigh.

7.6.4.2 Repeat the 180°C drying cycle for 15 minutes and desiccate for 30 minutes and weigh. The process needs to be repeated until a constant weight is obtained or until the weight loss is 0.5 mg or < 4% previous weight, whichever is less.

Note: The balance used for TDS and VDS is interfaced directly with TALS. Prior to starting the initial taring of the sample crucibles, start a TALS ADII batch and scan the sample IDs into it. As weights are taken, they are electronically recorded directly into the appropriate cells in the ADII batch.

7.6.5 If VDS are to be measured, transfer the method blank and sample crucibles containing the residue from the above procedure to a pre-heated muffle furnace at 550 ± 50°C for 15-20 minutes. Cool in a desiccator for at least an hour, and then weigh. Repeat the ignition/cooling cycle until the weight loss is within 4% of the previous weight. Do not overload the desiccator.

7.7 Documentation

7.7.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

7.7.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

7.7.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs are scanned and attached to the Documents section in the LIMS analytical batch.

7.7.4. Record all sample results and associated QC directly into LIMS. Level I and Level II reviews are performed in LIMS.

Examples of items included in the above reviews are as follows:

- QC data are outside the specified control limits for accuracy and precision
- Unusual detection limit changes are observed
- Samples having unusually high results
- Samples exceeding a known regulatory limit
- Raw data indicating some type of contamination or poor technique
- Transcription errors

8.0 QUALITY CONTROL

8.1 QC Summary

8.1.1 One MB and one LCS will be included in each laboratory lot of 20 samples. The MB will be examined to determine if contamination is being introduced in the laboratory. The LCS will be examined to determine accuracy which will be measured by the percent recovery (%R). The recovery must be in range, as determined by in-house control limits or statistical analysis, in order to be considered acceptable. Additionally, %R will be plotted on control charts to monitor method accuracy. Precision will be measured by the reproducibility of LCSs between batches.

8.1.2 One MS is done per batch of 20 samples. Acceptance limits of 75-125% are applied.

8.1.3 One Matrix Duplicate is done per 10 samples. The Standard Methods limit of 5% RPD will be applied to the matrix duplicate.

8.2 Corrective Actions

When an out of control situation occurs, the analysts must use their best analytical judgment and available resources to determine the corrective action to be taken. The out of control situation may be caused by more than one variable. The analyst should seek the assistance of their immediate supervisor, QA personnel, or other experienced staff if they are uncertain of the cause of the out of control situation. The test must not be resumed until the source of the problem and an in-control status is attained. All samples affected by the out of control situation should be reanalyzed. Out of control data must never be released without approval of the supervisor, QA personnel or the lab manager.

Listed below are steps that must be taken when an out of control situation occurs:

- demonstrate that all the problems creating the out of control situation were addressed;
- document the problem and the action taken to correct the problem on the data review checklist;
- write an NCM (Non-Conformance Memo) and email it to the appropriate people for review;
- receive approval (signature) of the Supervisor, Technical Director, QA personnel, or the Laboratory Director prior to the release of any analytical data associated with the problem.

Suggested Actions to specific out of control situations:

8.2.1 Laboratory Control Sample (LCS)

- reanalyze the LCS to verify that an out of control situation exists;
- determine the source of error within the preparation procedure, correct the problem and repeat the sample set. (Sources of contamination could be the reagents, the LCS stock solution, or the preparation area.)
- document all situations on the data review check list and write an NCM.

8.2.2 Method Blank (MB)

- reweigh the MB to verify contamination at a level > Reporting Limit;
- determine the source of contamination and correct the problem;
- all samples whose concentration are above the RL, but <10 times the elevated MB level must be reprocessed and reanalyzed; any sample which is >10 times the MB level need not be reanalyzed. However, the blank will be flagged and documented on the data review checklist and an NCM must be written.

8.2.3 Matrix Duplicate (DU)

- the sample will be flagged if the RPD between the duplicates is >5%. However, if the difference between the duplicates is ± the Reporting Limit, the duplicates are acceptable, and no flag is required.
- the situation must be documented on the data review checklist and an NCM must be written.

8.2.4 Matrix Spike (MS)

- Report all spikes, whether or not they are in control. Out of control spike recoveries will result in data flags.
- Note out-of-control spikes on the data review checklist and write an NCM.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 TDS Residue, mg/L

$$\frac{(A - B) \times 1000000}{C}$$

Where:
A = weight of dried residue + dish (g)
B = weight of dish (g)
C = volume of sample used in mL

9.2 VDS, mg/L

$$\frac{(A - B) \times 1000000}{C}$$

Where:
A = weight of crucible and residue before ignition, grams
B = weight of crucible and residue after ignition, grams

9.3 Accuracy

9.3.1 LCS % Recovery

$$\frac{\text{observed concentration}}{\text{actual concentration}} \times 100$$

9.3.2 Matrix Spike % Recovery

$$\frac{(\text{spiked sample}) - (\text{unspiked sampled})}{\text{spike concentration}} \times 100$$

9.4 Precision

9.4.1 Matrix Dup. Relative Percent Difference (RPD)

$$\text{RPD} = \frac{|\text{orgi.sample value} - \text{dup. sample value}|}{\left[\frac{\text{orgi sample value} + \text{dup sample value}}{2}\right]} \times 100$$

10.0 Pollution Control

It is Eurofins policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

10.1 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to UP-WM-001.

The following waste streams are produced when this method is carried out.

- Any acidic sample waste generated by the analysis should be disposed of in the corrosive waste stream.
- Contaminated filter and filter residue generated by the analysis should be disposed of in the non-hazardous white waste bins.

11.0 Method Performance Criteria

Refer to sections 1, 6, 7 and 8.

12.0 References

Refer to Section 1.0

13.0 ATTACHMENTS

N/A

14.0 REVISION HISTORY

- Revision 27 updated on 04/18/24
- Annual Review
- Section 1.0 added 23rd ED
- Section 4.0 updated equipment
- Section 7.3.2 added equivalent may be used
- Section 7.4 updated to balance calibration module and temperature being recorded in TALS
- Section 7.7 was rewrote and reformatted

TITLE: Wet Chemistry
Total Organic Carbon / Total Inorganic (Dissolved) Carbon

Approvals (Signature/Date):

Paul Kolarczyk 12-21-23
Paul Kolarczyk — Date
Supervisor, Wet Chemistry

Chris Hoham 12/21/23
Chris Hoham — Date
Env. Health & Safety Coor.

Nicole Berg 12/21/23
Nicole Berg — Date
Quality Assurance Manager

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1.0 SCOPE / APPLICATION

This Standard Operating Procedure is used to quantitatively determine the Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC), Total Inorganic Carbon (TIC), and Dissolved Inorganic Carbon (DIC) content in water matrices using either UV/persulfate oxidation or high-temperature combustion, followed by non-dispersive IR detection. Total Carbon and Inorganic Carbon may also be measured by setting up the instrument differently. This SOP was written using Standard Methods 5310C-00, 5310C-2011, 5310C-2014, 5310C-23rd Ed. and SW-846 Method 9060 and 9060A as references. The analyst also must reference the individual instrument Operations Manual.

On occasion, clients request slight modifications to this SOP. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP) and authorized via laboratory signature approval; and amended to the data packages case narrative. **Note: Method modifications are not allowed for Drinking Water samples without prior written approval from the US EPA.**

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL), also referred to as the detection limit (DL) in NELAC documents, is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants" with additional details are provided in the Eurofins Corporate SOP, *NDSC-QA-SOP42091, Detection and Quantitation Limits* and the Eurofins Chicago SOP, *UP-QA-017, Method Detection Limit Studies.* MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are performed and verified on an annual basis verifying the Lower Limit of Quantitation (LLOQ) for the method.

1.1.2 Demonstration of Capability

Before the laboratory may institute a new method and begin reporting results, the laboratory shall confirm that it can properly operate the method. A demonstration of capability is performed whenever there is a change in instrument type, method or personnel. An Initial Demonstration of Capability (IDOC) must be thoroughly documented and approved by the Department Manager/Supervisor and QA Manager prior to independently analyzing client samples. All associated documentation must be retained in the QA Department and in the Analyst Training files. For additional details on the demonstration of capability procedures followed, refer to the laboratory SOP, *UP-QA-QAM, Quality Assurance Manual, Sections 19.4.2 and 19.4.3.*

1.1.3 Reporting Limits (LLOQ)

Reporting Limits (LLOQ) are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. Because of the high level of quantitative error associated with determinations at the level of the MDL, the laboratory keeps the reporting limit higher than the MDL. Wherever possible, reporting is limited to values approximately 3-5x the respective MDL to ensure confidence in the value reported. Client specific requests for reporting to the MDL are special circumstances not to be confused with the previous statement.

Matrix	Reporting Limit
Waters	1.0 mg/L

The RLs are referred to as the Limit of Quantitation (LOQ) in NELAC documents. These documents also refer to the Level of Detection (LOD), which at Eurofins Chicago is set at ½ the LOQ.

1.1.4 Definitions

Refer to Section 3.0 of the Laboratory's Quality Assurance Manual (UP-QA_QAM).

1.2 Summary of Method

The measurement of TOC indicates the presence of organically bound carbon. Organic chemicals are of a primary environmental concern because of their wide spread industrial and agricultural uses. TOC analysis provides the basic screening measurement to warrant subsequent specific analyses if high TOC levels are found. DOC is determined by the same process, but on a filtered sample.

Samples are acidified to convert inorganic carbon, including carbonates and bicarbonates, to CO_2. Samples are then sparged with air or oxygen to remove all CO_2, including any CO_2 initially present in the sample, leaving only organic carbon in the sample. Organic carbon is then oxidized to carbon dioxide by either high-temperature combustion, or acidified persulfate in the presence of ultraviolet light. This carbon dioxide is carried to an infrared analyzer. A microprocessor calculates the area of the peaks produced by the analyzer, compares them to the peak area of the calibration standards stored in the memory, and prints out a calibrated organic carbon value in mg/L. TIC may be determined on the Fusion instrument by setting the instrument in TIC mode. In TIC mode the instrument bypasses the UV-persulfate oxidation and quantifies from the sparging step, against a previously run inorganic carbon curve. TIC may be determined on the Shimadzu instrument by running in the IC mode. DIC values are determined the same way, but on filtered samples.

Since some purgeable organics may be removed during the inorganics sparging step of this analysis, TOC as described in this SOP may be more correctly referred to as NPOC, or Non-Purgeable Organic Carbon.

1.2.1 Theory of Operation

Eurofins Chicago has 2 different TOC instruments (also see section 4.0):

Fusion: Liquid samples are introduced through a sipper probe on an automatic analyzer. TIC and TOC may be determined on the same sample. The inorganic carbonates are converted to CO_2 and measured by a Non-Dispersive Infrared Analyzer (NDIR) as TIC. The ultra-violet source is then activated and sodium persulfate is added to the elevated temperature reactor module to convert the organic carbon to carbon dioxide which is measured by the NDIR and is directly proportional to the TOC in the sample. Spent sample and reagents are purged from the unit and the next sample is then analyzed after an automatic system wash.

The "Static Pressure Concentration" builds up all the generated CO_2 to a certain pressure in the detector, which then takes a single reading. This is good for low level detection. When the replicate reading (TOC 2) is higher than the 1st (TOC1), it indicates that not all the gas was swept out of the detector. Normally this is only a problem with some difficult samples, and it can be compensated for by increasing the "baseline stabilization time" in the method. A second method can be set up only for difficult samples because it will increase the run time.

Shimadzu: TOC samples are acidified and sparged in the sample vial to remove inorganic carbon. Sample aliquots are then transferred into a combustion tube, which is filled with an oxidation catalyst and heated to 680ºC. All carbon is transformed to CO_2 and measured by a NDIR analyzer. TIC uses the same process, but the acidification and purging happens in the syringe inside the instrument. The purged CO_2 is collected and analyzed through the same combustion process as TOC. Total carbon may be analyzed by directly transferring the sample to the combustion tube without any acidification or sparging.

2.0 INTERFERENCES

- Persulfate oxidation is slowed in samples containing significant concentrations of chloride by the preferential oxidation of chloride. At a concentration of 0.1% chloride, oxidation of organic matter may be inhibited completely. This is why Eurofins Chicago prefers to analyze sulfuric acid-preserved samples.
- To obtain TOC results, carbonates and bicarbonates, positive interferences, must be completely removed by acidification and sparging of a clean gas (O_2 or N_2) to remove the CO_2.
- Excessive acidification of sample, producing a reduction in pH of the persulfate solution to 1 or less, can result in sluggish and incomplete oxidation of organic carbon.
- The intensity of the ultraviolet light reading the sample matrix may be reduced by highly turbid samples, resulting in sluggish or incomplete oxidation.
- Large organic particles or very large or complex organic molecules may be oxidized slowly because persulfate oxidation is rate limited.
- Improper sample handling and treatment is a likely source of contamination.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual, Lab Specific Addendum to the CSM, and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coat and closed-toe, nonabsorbent shoes are a minimum.

3.1 Specific Safety Concerns or Requirements

- The auto sampler has a probe that is sharp; use caution not to stick yourself.
- The UV reactor is hot and can cause burns if touched.
- The Sodium Persulfate is a strong oxidizer. Avoid contact with combustible materials, organic materials, strong reducing agents, and excess heat.
- The high-temp combustion chamber operates at 680ºC, care must be taken to cool the system completely prior to contact.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method.** The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydrator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
Phosphoric Acid	Corrosive	1 mg/m^3 TWA	Inhalation is not an expected hazard unless misted or heated to high temperatures. May cause redness, pain, and severe skin burns. May cause redness, pain, blurred vision, eye burns, and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm - Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sodium Persulfate	Oxidizer Corrosive	0.1 mg/m^3- TWA as Persulfates	Causes irritation to the respiratory tract. Symptoms may include sore throat, shortness of breath, inflammation of nasal passages, coughing, and wheezing. Causes severe irritation or burns to the skin and eyes. Symptoms include redness, itching, pain and burns. May cause allergic skin reactions. Can cause eye damage.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 EQUIPMENT AND SUPPLIES

- Teledyne-Tekmar Fusion TOC analyzer (known as TOC 5) with built-in carrousel autosampler and TekLink version 1.1.0.189 software on the accompanying PC
- Shimadzu TOC-L (TOC6) with ASI L autosampler and TOC Control L software version 1.06
- 40 mL VOA vials, with septa for the Fusion and the Shimadzu.
- Class A volumetric flasks: 100 mL, 200 mL, 1000 mL
- Eppendorf pipettes
- 5 mL Syringe with 0.45 µm filter disc for DOC analysis

5.0 REAGENTS AND STANDARDS

All standards and reagents are prepared with Milli-Q Water, unless otherwise specified. All standards and reagents are prepared in Class A volumetric glassware and stored at 4 ± 2 °C when required. Only reagent grade chemicals meeting ACS criteria are to be used.

5.1 Reagents

5.1.1 Acids

- Phosphoric acid, concentrated
- Sulfuric acid, concentrated, 50%
- Hydrochloric acid, concentrated

5.1.2 Sodium Persulfate

Dissolve 25 grams of sodium persulfate in 213 mL of Milli-Q water and add 9 mL of concentrated phosphoric acid. Double or triple the preparation as required. It is best to prepare this reagent at least one day in advance of its use.

- Life of Reagent: 1 – year
- Storage Requirements: None

5.1.3 21% Phosphoric Acid

Add 37 mL of concentrated phosphoric acid to 188 mL of Milli-Q water.

- Life of Reagent: 1 – year
- Storage Requirements: None

5.1.4 1M Hydrochloric Acid

Slowly add 83 mL of concentrated hydrochloric acid to a 1.0 L volumetric flask containing ~800 mL of Milli-Q water. Cool and dilute to volume with Milli-Q water.

- Life of Reagent: 1 – year
- Storage Requirements: None

5.1.5 CO2 Absorber

Soda lime canister from Shimadzu.

5.2 Standards

5.2.1 TOC Stock I, 2000 mg/L

5.2.2 TOC Stock II, 2000 mg/L

On a balance capable of reading 0.1 mg, weigh out 425 mg of reagent grade potassium hydrogen phthalate dried to a constant weight and desiccated, transfer quantitatively with DI water to a 100 mL Class A volumetric flask, dissolve, and add 0.1 mL of concentrated sulfuric acid. Dilute to volume with DI water.

- Life of Standard: 1 – month
- Storage Requirements: Glass amber bottle

*Stock II is prepared as Stock I **EXCEPT** an alternate stock source is used.

5.2.3 TIC Stock I, 2000 mg/L

In a 100 mL volumetric flask, dissolve 1.7666 g sodium carbonate in freshly boiled and cooled Milli-Q water.

- Life of Standard: 1 – month
- Storage Requirements: Glass amber bottle stored in the refrigerator

5.2.4 TIC Stock II, 1000 mg/L

In a 100 mL volumetric flask, dissolve 0.35 g sodium bicarbonate and 0.4418 g sodium carbonate in freshly boiled and cooled Milli-Q water.

- Life of Standard: 1 – month
- Storage Requirements: Glass amber bottle stored in the refrigerator

5.2.5 Calibration Curve

Using Eppendorf pipettes, prepare the calibration curve by diluting the stock I standard as listed below with a final volume of 200 mL with DI water. Calibration standards must be prepared monthly.

Concentration	Volume (uLs) Stock I (Rgt. 5.2.1)
0	0
1	100
5	500
10	1000
15	1500
20	2000
30	3000
40	4000

NOTE: For TIC/DIC, prepare the curve using the same volume of standard as TOC but use the TIC Stock I (Rgt. 5.2.3).

5.2.6 Matrix Spike (MS) / MS Duplicate (MSD) Sample, 10 mg/L

Prepare fresh prior to each use.

TOC/DOC: Dilute 0.5 mL of TOC Standard II (Std. 5.2.2) to 100 mL with sample. Alternatively, add 200 uL of TOC Standard II to 40 mL of sample.

TIC/DIC: Dilute 1.0 mL TIC Standard II (Rgt. 5.2.4) to 100 mL with sample. Alternatively, add 400 uL of TIC Standard II to 40 mL of sample.

5.2.7 Initial and Continuing Calibration Verification (ICV); 20 mg/L

TOC/DOC: Dilute 2 mL of TOC Stock II, Rgt. 5.2.2, for the ICV, or TOC Stock I, Rgt. 5.2.1, for the CCV into a 200 mL volumetric flask. Dilute to volume with Milli-Q water acidified with 0.2 mL sulfuric acid. Prepare weekly.

TIC/DIC: Dilute 4 mL of TIC Stock II, Rgt. 5.2.4, for the ICV, or TIC Stock I, Rgt. 5.2.1, for the CCV, into a 200 mL volumetric flask. Dilute to volume with Milli-Q water. Do not preserve. Prepare daily.

5.2.8 Continuing Calibration Verification (CCV);

There are 3 levels for the CCV to prepared and analyzed on a rotating basis. The CCVs are to be prepared weekly.

5.2.8.1 Low Level CCV (CCVL)

TOC/DOC: Dilute 0.1 mL of TOC Stock I (Rgt. 5.2.1) into a 200 mL volumetric flask. Dilute to volume with Milli-Q water acidified with 0.2 mL sulfuric acid. Prepare weekly.

TIC/DIC: Dilute 0.1 mL of TIC Stock I (Rgt. 5.2.3) into a 200 mL volumetric flask. Dilute to volume with Milli-Q water. Prepare fresh prior to each use.

5.2.8.2 Mid-Level CCV

TOC/DOC: Dilute 1 mL of TOC Stock I (Rgt. 5.2.1) into a 200 mL volumetric flask. Dilute to volume with Milli-Q water acidified with 0.2 mL sulfuric acid. Prepare weekly.

TIC/DIC: Dilute 1 mL of TIC Stock I (Rgt. 5.2.3) into a 200 mL volumetric flask. Dilute to volume with Milli-Q water. Prepare fresh prior to each use.

5.2.8.3 High Level CCV (HCCV)

TOC/DOC: Dilute 3 mL of TOC Stock I (Rgt. 5.2.1) into a 200 mL volumetric flask. Dilute to volume with Milli-Q water acidified with 0.2 mL sulfuric acid. Prepare weekly.

TIC/DIC: Dilute 3 mL of TIC Stock I (Rgt. 5.2.3) into a 200 mL volumetric flask. Dilute to volume with Milli-Q water. Prepare fresh prior to each use.

5.2.9 Initial / Continuing Calibration Blank (ICB / CCB)

TOC / DOC: Milli-Q water acidified with sulfuric acid at 0.1 mL per 100 mL (40 uL per 40-mL vial.)

TIC / DIC: Milli-Q water. Do not acidify.

5.2.10 Laboratory Control Sample (LCS), 10 mg/L

TOC: Dilute 1.0 mL of Stock Organic Carbon Standard II (Std. 5.2.2) into a 200 mL volumetric flask. Dilute to volume with Milli-Q water, acidified with 0.2 mL sulfuric acid.

TIC/DIC: Dilute 2.0 mL of TIC Standard II (Rgt. 5.2.4) into a 200 mL volumetric flask. Dilute to volume with Milli-Q water. Do not acidify.

5.2.11 TIC standard for TOC/DOC batches, 10 mg/L

Dilute 2.0 mL of TIC Standard II (Rgt. 5.2.4) into a 200 mL volumetric flask. Dilute to volume with Milli-Q water. Do not acidify. Prepare daily.

Note: This standard is analyzed near the beginning of each TOC/DOC batch to verify that the analyzer is in the correct mode and that the inorganic sparger is working properly.

6.0 CALIBRATION (NON-DAILY)

A multi-point calibration curve is used for organic and inorganic carbon analyses. The linearity must be confirmed at least monthly by running a linear range curve with a blank and concentrations which cover the anticipated range of measurement (refer to Section 5.2.5). One of the calibration standards will be at or below the desired reporting limit.

If a correlation coefficient of ≥ 0.995 is not met, the instrument will be recalibrated prior to analysis of samples. Calibration data, to include the correlation coefficient a PDF copy is attached to each batch and kept with the sample data to maintain a permanent record of instrument calibrations.

The ICVs and CCVs are analyzed daily to confirm linearity.

7.0 PROCEDURE

7.1 Quality Control Checks

Quality Controls	Frequency	Control Limit
Method Blank (MB)	1 in 20 samples	< Reporting Limit, < ½ Reporting Limit (per QAPP) < MDL (Drinking Water)
LCS	1 in 20 samples	86 - 116% (Statistical) 80 - 120% (QAPP) [1]
LCS Duplicate (LCSD) [2]	1 in 20 samples	≤ 20 RPD
Matrix Duplicate (DU)[3,5]	1 in 20 samples	≤20 RPD
Injection replicates	All samples	Smp Conc ≥ RL +/- 10% limit[6] Smp Conc < RL +/- MDL limit
Matrix Spike (MS/MSD) [4,5]	1 in 10 samples	75-125%[1], 80-120% (per QAPP)

All TOC water samples are analyzed in quadruplicate.
Blanks and quality control samples in the above table are analyzed in duplicate.

[1] In-house statistical limits or individual QAPP limits may be required rather than those in the table. Refer to the paper work accompanying a project's in-house chain-of-custody for appropriate limits to use for each sample.
[2] The reading of a second LCS, in quadruplicate, is optional and specifically not needed for some clients. Refer to the paper work accompanying a project's in-house chain-of-custody for appropriate QC requirements.
[3] DUs are performed as requested by the client/project.
[4] When analyzing for method SW-846 9060, an MS/MSD must be analyzed on 1 in 10 samples.
[5] The sample selection for MS/MSD or DU is rotated among client samples so that various matrix problems may be noted and/or addressed.
[6] Repeat injection until consecutive measurements are obtained that are reproducible to within +/- 10% for compliance samples.

7.2 Sample Preservation and Storage

Holding time, preservation techniques and sample container may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client request. Listed below are the holding times, and the references which include container and preservation requirements for compliance with the Clean Water Act (CWA).

Regulation	Holding Time	Preservation	Reference
CWA	28 days	pH<2 (sulfuric acid – 5310C; 9060A); pH<2 (phosphoric acid - 5310C) Cool 4 ± 2°C (HCl is approved (9060A), but not preferred at Eurofins Chicago – See Sec. 2.0)	40CFR, Part 136.3

7.3 Sample Preparation

The TOC sample vial is not opened prior to analysis, therefore, the pH of the sample is checked with pH indicator paper after analysis to verify proper preservation at the time of sampling. pH is to be documented, ff the pH of a sample is not <2, further documentation in an NCM is required, which is then forwarded to the project manager.

The VOA vial is shaken to homogenize the sample prior to loading on the instrument autosampler.

If the sample appears dirty or has a strong odor, the sample usually contains a high amount of TOC and is to be diluted prior to its initial analysis to avoid overloading the infrared analyzer or clogging instrument tubing. The sample must be homogenized prior to taking an aliquot out for the dilution, which then must be preserved with concentrated sulfuric acid. Should a diluted sample display a TOC result below the reporting limit, the sample is reanalyzed at a lesser dilution or at full strength. All analysis must be retained as raw data, and all dilutions must be justified.

If dissolved organic carbon (DOC) is to be determined and the sample was not field filtered, filter an unpreserved portion of the sample into 2, 40 mL glass vials using a pre-rinsed 5 mL syringe with 0.45 µm filter disc. If necessary due to a high concentration of solids, use a vacuum filtration device, and then dispense the filtrate into the 2, 40 mL vials. Completely fill the vials. Preserve each vial with 40 uL of sulfuric acid. The filtration and acidification should be done as soon as possible after receipt at the laboratory, not to exceed 48 hours from collection, per 40 CFR part 141.131. After filtration and acidification, the sample must still be analyzed within 28 days of collection.

7.4 Calibration / Standardization

Instrument calibration consists of the two types: Initial Calibration and Continuing Calibration. Initial Calibration establishes the calibration range of the instrument and determines the instruments response over that range. Refer to the Eurofins Corporate Policy for Calibration Curves and the Selection of Calibration Points (NDSC-QA-QP44940) *and the Selection of Calibration Points* and the *Calibration Criteria Training, Inorganics* Document CHI-22-09-472 for further guidance.

Continuing Calibration used within an analytical sequence to verify stable calibration throughout the sequence, and/or to demonstrate that the instrument response did not drift during a period of non-use of the instrument.

Calibration Controls	Frequency	Control Limit
Reagent/Acid Blank	When Reagent/Acid is changed	Reagent abs. <7; Acid abs. <3 recommended
TIC standard	One in every run	< Reporting Limit
Calibration Curve (Linear – 1st Order)	Monthly or as needed; prior to samples	r ≥ 0.995 x-intercept < Reporting Limit
ICV	After calibration	90 – 110%
CCV	After every 10 samples (rotate concentration)	50-150% (Low level) 85-115% (mid and high level)
ICB / CCB	every 10 samples; end of sequence	< Reporting Limit, < ½ Reporting Limit (per QAPP)
MRL	Per Program / QAPP	

Note: Calibration check standards and blanks are analyzed with a single analysis.

7.5 Preventive Maintenance

Follow the individual instrument manual recommendations for preventive maintenance. Refill all water containers. Document the daily maintenance and any “as needed” maintenance in the instrument maintenance logbook for each instrument on each day of operation. A “return to control” must be documented for any out of control event which required instrument maintenance to achieve method compliance.

Non-Routine Maintenance may include the following and would be performed prior to sample analysis on an as needed basis:

- Copper and Tin Pellet replacement - Fusion
- UV Lamp / Glassware cleaning - Fusion
- Copper and Tin Glass Tube cleaning - Fusion
- regeneration or replacement of catalyst - Shimadzu
- replace CO_2 absorber - Shimadzu

Copper column replacement - Shimadzu

Return to Control Documentation should include the AD Batch Number and the acceptable LCS % Recovery observed for the 1st batch following the maintenance.

Maintenance performed by outside vendors must also be documented in the maintenance log. The Vendor's written documentation of the maintenance must be stapled into the maintenance logbook manually.

7.6 Sample Analysis

Each sample is prepared by the instrument (e.g. inorganic carbon removal) and multiple aliquots are analyzed by the instrument to obtain a reproducible measurement. Follow the individual analyzer manual for instructions for setting up the computer and operating the instrument. The vials for the Shimadzu instrument may only be filled about 2/3 full to allow for direct acidification and sparging in the sample vial.

7.7 Documentation

7.7.1 Instrument Print-out

The sequence of analysis of the samples and standards is contained in the instrument summary print-out, which serves as the analysis log. The analyst must note recoveries on the print-out, and carefully cross out unused data, being careful to document the reason and data is not reported.

7.7.2 Traceability of Standards

Upon receipt or preparation, each chemical salt, solvent, acid, standard, or other reagent is entered into TALs LIMS and is issued a unique ID#. Further information entered into the database includes the manufacturer, lot # (if applicable), the date received or prepared, the expiration date, volume/weight received; concentration (if applicable); preparation details (if applicable), initials of the recording analyst, and the description of the item (i.e., TOC Stock Solution – LCS). Once the record is created, a unique label is printed and affixed to the appropriate standard/reagent container.

7.7.3 Data Review

Analytical data goes through a 200% review cycle. As results are generated, analysts review their work to ensure that the results generated meet QC requirements and relevant EPA methodologies. The analyst transfers the data into TALs in the Analyst Desktop module. Where non-compliance is observed, the analyst creates Non-Conformance Memos (NCMs) in TALs. Flags and data qualifiers can be method, project, program or QAPP specific. The analyst documents the initial review and sets the batch status in LIMs to 1st level review. The second level or peer review of the data is conducted by another individual who has been trained on the review process. This secondary review is documented in the same batch, making any necessary corrections to the data or additions to the NCMs as necessary. The batch is then set to 2nd level review. The raw data, including the instrument print-outs, and manual entries, and electronic files are retained for easy retrieval in accordance with the laboratory's record and retention policy outlined in the SOP, *UP-QA-QAM, Section 16*.

Examples of items included in the above reviews are as follows:

- QC data are outside the specified control limits for accuracy and precision
- Unusual detection limit changes are observed
- Samples having unusually high results
- Samples exceeding a known regulatory limit
- Raw data indicating some type of contamination or poor technique
- Transcription errors
- Results outside of calibration range

8.0 QUALITY CONTROL

8.1 QC Summary

8.1.1 One MB and one LCS will be included in each laboratory lot of 20 or fewer samples. The MB will be examined to determine if contamination is being introduced in the laboratory. The LCS, when prepared in duplicate (duplicate is labeled LCSD) as required by the client and/or QAPP, will be examined to determine both accuracy and precision.

8.1.2 Accuracy will be measured by the percent recovery (%R) of the LCS. The recovery must be in range, as determined by in-house control limits or statistical analysis, in order to be considered acceptable. Additionally, %R will be plotted on control charts to monitor method accuracy.

8.1.3 Precision will be measured by the reproducibility of both LCS injections for each analysis, but will only be statistically generated for LCS data. Results must agree within in-house control limits or statistical control limits (if required) in order to be considered acceptable.

8.1.4 The replicate injections of the same sample must be within +/- 10%, for sample concentrations ≥ RL of 1.0 mg/L and +/- the MDL for sample concentrations < RL of 1.0 mg/L. Note: The replicate injections must be within 10% for all compliance samples above the LOQ for the state of Wisconsin.

8.1.5 One MS, read in duplicate is analyzed per matrix per 20 samples for SM 5310B-00 and 5310C-00. One MS is analyzed per 10-sample analytical set for SW 9060 or 9060A. Results must agree within the in-house precision/accuracy limits (see table in section 7.1) or statistical control limits if required in order to be considered acceptable.

8.2 Corrective Action

When an out-of-control situation occurs, the analysts must use their best analytical judgment and available resources to determine the corrective action to be taken. The out-of-control situation may be caused by more than one variable. The analyst should seek the assistance of their immediate supervisor, QA personnel, or other experienced staff if uncertain of the cause of the out-of-control situation. The test must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out of control situation should be reanalyzed. Out-of-control data must never be released without approval of the Wet Chemistry Supervisor, Inorganics Manager, Project Manager, QA personnel or the Laboratory Director.

Listed below are steps that MUST be taken when an out-of-control situation occurs:

- demonstrate that all the problems creating the out-of-control situation were addressed;
- document the problem and the action which was taken to correct the problem in the logbook;
- document in the logbook that an in control status has been achieved; and
- receive approval (signature) of the Wet Chemistry Supervisor, Inorganics Manager, Project Manager, QA personnel or the Laboratory Director prior to the release of any analytical data associated with the problem.

Suggested Actions to specific out of control situations (all reported data associated with the following should have an NCM written in AD):

QC Standard	Suggested Corrective Actions
Calibration Curve	• reanalyze the standard curve; • prepare new stock and/or working standards; • check reagents/solutions and prepare fresh if necessary.
Initial Calibration Verification (ICV)	• repeat to verify proper preparation; • prepare new ICV from original stock; • check for instrument base-line drift; • restandardize with existing standards, reanalyze; • check reagents/solutions and prepare fresh if necessary; • prepare new stock and/or working standards and recalibrate;

QC Standard	Suggested Corrective Actions
TIC Standard in TOC/DOC batches	• check instrument mode and reagent levels
Initial Calibration Blank (ICB)	• prepare a new ICB to verify proper preparation; • verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability; • determine the source of contamination by the process of elimination, correct the problem and reanalyze. (Carry over from a previous analysis or reagent contamination are two common sources).
Laboratory Control Sample (LCS)	• reanalyze to verify that an out of control situation exists; • determine the source of error within the preparation procedure, correct the problem and repeat the sample set. Sources of contamination could be the reagents, the LCS stock solution, or the preparation area. **NOTE:** When LCS(s) is high, any samples that are less than the reporting limit may be reported. Precision: LCS and LCD must meet the control limits of ≤ 20% RPD. If this criteria is not met, and both LCS's meet the % Recovery control limits, then see your supervisor for proper corrective action.
Method Blank (MB)	• reanalyze to verify contamination at a level greater than the reporting limit; • determine the source of contamination and correct the problem; • all samples whose concentration is <10x the MB level must be reprocessed and reanalyzed; • any sample which is >10x the MB level need not be reanalyzed; however, the situation must be documented with a NCM written.
Matrix Duplicate (DU)	• the sample must be reprocessed and reanalyzed unless the sample concentration is <5x reporting Limit, then the ± Reporting Limit rule applies; • if the reanalysis is within the control limits, the second value is reported; • The situation must be documented with a NCM and approved by your supervisor.
Matrix Spike (MS)	• If a single spike is done and it is outside the acceptance limits, it must be repeated to verify the matrix effect. • Report all spikes, whether or not they are in control. • Note out-of-control spikes with a NCM
Continuing Calibration Verification (CCV/CCVL/CCVH)	• reanalyze to verify proper preparation; • prepare new CCV from original stock; • check for instrument base-line drift; • check reagents/solutions and prepare fresh if necessary; • recalibrate with a new standard curve and repeat all samples since the previous in control CCV; • never dispose of any samples until you are sure that all QC are within designated control limits.
Continuing Calibration Blank (CCB)	• prepare a new CCB to verify proper preparation; • verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc.; • determine the source of contamination by the process of elimination, correct the problem and reanalyze all the samples since the previous in control CCB. (Carry over from a previous analysis and reagent contamination are two common sources). • never dispose of any samples until you are sure that all QC are within their designated control limits.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 Sample Results

The individual results from each duplicate or quadruplicate analysis are read directly from the instrument printer and entered into TALS. The replicate results must meet precision requirements. The individual results as well as the mean result may be reported, according to client requirements.

9.2 Accuracy

9.2.1 ICV/CCV, LCS % Recoveries

$$\frac{\text{Observed Concentration}}{\text{Spiked Concentration}} \times 100$$

9.2.2 MS % Recovery

$$\frac{(\text{Spike sample result}) - (\text{Unspiked sample result})}{\text{Spike Concentration}}$$

9.3 Precision

Matrix Duplicate and LCSD (when required) Relative Percent Difference (RPD):

$$\text{RPD} = \frac{|\text{Orig. sample value} - \text{dup. sample value}|}{[\frac{\text{Orig. sample value} + \text{dup sample value}}{2}]} \times 100$$

*For calculating duplicates and MSs, the original sample value is the average of the replicate/quadruplicate results of the sample.

10.0 POLLUTION CONTROL

It is Eurofins policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

10.1 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to UP-WM-001.

- Waste from this procedure will enter the ‘Corrosive Wastestream’.

11.0 METHOD PERFORMANCE CRITERIA

Refer to Sections 1, 6, 7 and 8.

12.0 REFERENCES

Refer to Section 1.

13.0 ATTACHMENTS

None.

14.0 REVISION HISTORY

- Revision 26 updated on 12/21/23
- Annual Review
- Section 1.1.1 updated corporate SOP.
- Throughout removed reference to data review checklist and data cover page also removed corresponding attachments.
- Section 1.0 updated to include SM 5310C-23rd Ed. for reference.
- Section 5.2.5 simplified chart
- Section 5.2.8 added different level CCVs
- Section 7.1 updated to specify all samples are ran in quadruplicates and remove SC note
- Section 7.5 removed reference to attachment
- Section 7.4 CCV criteria was added and corrected
- Section 8.2 All concentration levels of CCVs added to chart

TITLE: Wet Chemistry
Total and Volatile Suspended Solids

Approvals (Signature/Date):

Logan Poracky 8/2/24
Logan Poracky — Date
Supervisor, Wet Chemistry

Chris Hoham 8/2/24
Chris Hoham — Date
Env. Health & Safety Coor.

Nicole Berg 8/2/24
Nicole Berg — Date
Quality Assurance Manager

Paul Kolarczyk 8-2-24
Paul Kolarczyk — Date
Inorganic Technical Manager

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1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) is used to determine the total non-filterable residue content in drinking, surface, and ground waters, domestic and industrial liquid wastes. This SOP was written using the following methods as references:

- Total Suspended Solids (TSS): Standard Methods 2540D-1997, 2540D-2011, 2540D-2015 and 2540D-2020.
- Volatile Suspended Solids (VSS): Standard Methods 2540E-1997, 2540E-2011, 2540E-2020. & EPA 160.4 (91).
- QC requirements for TSS are found within the method itself and in Standard Methods, 2020-10, Sections A and B.

On occasion, clients request slight modifications to this SOP for non-drinking water samples. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP) where applicable, authorized via laboratory signature approval, and mentioned in the data package's case narrative. Note: There are no method modifications allowed for Drinking Water samples without prior written approval from the US EPA.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants" with additional details are provided in the Eurofins Corporate SOP, *NDSC-QA-SOP42091, Detection and Quantitation Limits* and the Eurofins Chicago SOP, *UP-QA-017, Method Detection Limit Studies.* MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; the MDL will be performed and verified on an annual basis verifying the Lower Limit of Quantitation (LLOQ) for the method

1.1.2 Demonstration of Capability

Before the laboratory may institute a new method and begin reporting results, the laboratory shall confirm that it can properly operate the method. A demonstration of capability is performed whenever there is a change in instrument type, method or personnel. An Initial Demonstration of Capability (IDOC) must be thoroughly documented and approved by the Department Manager/Supervisor and QA Manager prior to independently analyzing client samples. All associated documentation must be retained in the QA Department and in the Analyst Training files. For additional details on the demonstration of capability procedures followed, refer to the laboratory SOP, *UP-QA-QAM, Quality Assurance Manual, Sections 19.4.2 and 19.4.3.*

1.1.3 Reporting Limits (LLOQ)

Reporting Limits (LLOQ) are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. The laboratory maintains RLs that are higher than the MDL. Wherever

possible, reporting is limited to values ~3-5x the respective MDL to ensure confidence in the value reported.

Test	Reporting Limit [1,2]
TSS / VSS	5.0 mg/L

[1] Based on a 500 mL minimum sample volume.
[2] Reporting limits will vary depending on sample/limited sample volume and dilution factors.

1.1.4 Definitions

Refer to Section 3.0 of the Laboratory's Quality Assurance Manual (UP-QA_QAM).

1.2 Summary of Method

Suspended solid matter in natural or man-made water bodies is of environmental importance because the presence of such material decreases the amount and depth of light penetration to the water body. The decrease in light penetration then decreases the potential for productivity of zooplankton and phytoplankton of the water body, limiting the available food sources to higher vertebrates and invertebrates that are necessary to keep the ecosystem in balance.

Wastewater treatment plant operators use this information as a guide to pump performance within the plant and can often troubleshoot potential future problems. Final effluents are monitored to evaluate overall plant performance as well as to provide estimations of the suspended solids loading to the receiving stream.

Suspended solids material occurs naturally as silt, leaves, etc., and is caused by a variety of naturally occurring processes such as rain, decay, animal activities, etc. Litter and industrial effluents are sources of manmade suspended solids pollutants.

Suspended solids are those particles that are easily removed by filtration and are retained by a micro-fiber filter. The type of filter holder, the pore size, porosity, area and thickness of the filter and the physical nature, particle size and amount of material deposited on the filter are the principal factors affecting the trapping of suspended solids materials. The residue remaining on the filter paper is dried to a constant weight at 103-105°C. If the TSS is < Reporting Limit, then VSS will not need to be determined.

2.0 INTERFERENCES

- Exclude large floating particles or submerged agglomerates of non-homogeneous materials from the sample if they are not representative of the sample.
- Because excessive residue on the filter may form a water-entrapping crust, limit the sample size to that yielding no more than 0.200 g (200 mg) of residue.
- For samples high in dissolved solids, thoroughly wash the filter to ensure removal of dissolved material.
- Prolonged filtration times resulting from filter clogging may produce high results owing to excessive solids caught on the clogged filter.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual, Lab Specific Addendum to the CSM, and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of

the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coat and closed-toe, nonabsorbent shoes are a minimum.

3.1 Specific Safety Concerns or Requirements

- Care should be taken when removing heated crucibles from the oven. Heat resistant gloves or tongs should be used when removing crucibles or racks.
- Diatomaceous earth contains silica. Dust may be hazardous to lungs and respiratory tract.
- Oily samples or those that contain volatile chemicals may ignite within a muffle furnace. In the case of a fire, the muffle furnace should be turned off and allowed to cool before the samples are removed and put under a hood.
- Extreme care should be used when using a muffle furnace, as temperatures are extremely high. Gloves designed for dealing with extreme temperatures must be used when handling any samples or glassware that has been in a muffle furnace.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit[1]	Signs and symptoms of exposure
Diatomaceous Earth	Carcinogen	10 mg/m^3	Warning harmful if inhaled. Causes irritation to skin eyes and respiratory tract. May affect lungs. Cancer hazard. Contains crystalline silica which can cause cancer. Risk of cancer depends on duration and level of exposure
[1] – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 Equipment and Supplies

- Analytical Balance - capable of weighing to 0.1 mg
- 103-105˚C oven
- Desiccator
- Various Class A graduated cylinders
- Vacuum Filtration Apparatus with clean metallic or non-metallic filter support
- Environmental Express ProWeigh™ Filters 47mm or Whatman™ 47mm934-AH™ RTU pre-prepared and weighed filters, with a pore size of 1.5 µm.
- 10 mL wide-bore disposable pipettes. Note: The calibration of each Lot# of pipettes are to be verified to the Class A specified limits of 1% RSD and 2% Tolerance using the spreadsheet (CHI-22-09-467) located in the W:\QC\WetChemistry directory. The Lot # of the pipette is to be written on the individual pipette bag if it is removed from its original vendor container/box. When used, the lot number of the pipette used for analysis must also be documented in the batch information screen in the TALs batch.
- Stir Plate
- Timer

5.0 REAGENTS AND STANDARDS

5.1 Stock Standards

5.1.1. Stock standards are purchased from an approved vendor. If no expiration date is provided, the stock standard solutions may be used for up to one year from open date and must be replaced sooner if verification from an independent source indicates a problem.

5.2 Intermediate / Working Standards

5.2.1. Intermediate / Working standards are prepared as dilutions from the stock standards. Intermediate / working standard solutions shelf life and are stored according to table below.. The intermediate / working standard solution must be replaced if verification from an independent source indicates a problem. Refer to the LIMS standards and reagents module for further details on preparation of intermediate / working standard solutions.

Reagent	Shelf life	Storage Requirement
TSS Stock solution 1 (200 mg/L)	5 days	None
TSS Stock solution 2 (100 mg/L)	1 week	None

5..2.2 TSS Standard for Method Detection Limit Study, 5.0 mg/L

On a balance capable of reading 0.0001 g (0.1 mg), weigh out 0.010 g (10 mg) of diatomaceous earth that has been dried at 103-105°C and desiccated, to the nearest 0.001 g (1 mg). Add it to approximately a liter of DI water in a 2.0 L Class A volumetric flask. Mix by inversion and dilute to volume with DI water. This is to be used for the quarterly MDL study, where a 500 mL aliquot is required for analysis.

5..2.3 TSS Standard for Method Detection Limit Study, 2.5 mg/L

On a balance capable of reading 0.0001 g (0.1 mg), weigh out 0.0025 g (2.5 mg) of diatomaceous earth that has been dried at 103-105°C and desiccated, to the nearest 0.001 g (1 mg). Add it to approximately 500 mL of DI water in a 1.0 L Class A volumetric flask. Mix by inversion and dilute to volume with DI water. This is to be used for the MDL check for the quarterly MDL study, where a 500 mL aliquot is required for analysis.

5.5 Batch QC

5.5.1 Method Blank (MB)

500 mL DI water

5.5.2 Laboratory Control Sample (LCS) 200 mg/L

200 mL of Stock Solution 1 (Rgt. 5.1).

5.5.3 Matrix Spike (MS); 100 mg/L

Pour 100 mL of Stock Solution 2 (Rgt. 5.2) through the same filter as the sample to be spiked. If possible, spike 100 mL of sample for a spike concentration of 100 mg/L.

NOTE: There is no MS or LCS for VSS. Only a MB and a Matrix Duplicate (DU) can be analyzed.

5.5.4 Matrix Duplicate (DU)

Duplicate of one sample. Not routinely analyzed.

6.0 CALIBRATION (NON-DAILY)

Not Applicable.

7.0 PROCEDURE

7.1 Quality Control

Quality Controls	Frequency	Control Limit
MB	1 in 20 samples	< Reporting Limit < MDL (Drinking Water)
LCS [1]	1 in 20 samples	80 – 120% Recovery
MS/MSD [2]	1 in 20 samples	75 – 125% Recovery, ≤20 RPD
DU [2]	1 in 10 samples	≤ 5 RPD

[1] LCS Duplicate (LCSD) is done only when insufficient sample is available for matrix QC or when requested by the client/project/contract.
[2] The sample selection for matrix QC, unless specified by the client on the chain-of-custody, is rotated among client samples so that various matrix problems may be noted and/or addressed. Note: An MS/MSD per batch is routinely done, but client-specific QAPPs may require a duplicate and a spike.

7.2 Sample Preservation and Storage

Holding time, preservation techniques and sample container may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client request. Listed below are the holding time and the reference, which includes container and preservation requirements for compliance with the Clean Water Act (CWA).

Regulation	Holding Time	Preservative	Reference
CWA (NPDES)	7 days	Cool 4 ± 2°C	40 CFR Part 136.3

Note: For EPA holding times expressed in days, Eurofins Chicago considers the expiration to be at the end of the last day. Some clients specifically require the holding time to be calculated to the hour, which will be noted on the analyst's backlog.

7.3 Sample Preparation

7.3.1 Sample Size

Working sample size varies. Generally 200 mL is sufficient, however, it is required that the sample volume be increased to obtain at least 0.0025 g (2.5 mg) of residue, or decreased so as to not exceed 0.200 g (200 mg). Standard Methods states to use up to 1.0 liter of sample volume to obtain the minimum residue, but the Eurofins Chicago RL of 5.0 mg/L is based on 500 mL of sample. Eurofins Chicago will meet client needs for lower RLs where applicable.

7.3.2 Filter Preparation

Environmental Express ProWeigh™ Filters 47 mm or Whatman™ 47mm934-AH™ RTU pre-prepared and weighed filters are supplied in individual aluminum dishes, and are already rinsed, desiccated, and pre-weighed. The weight from one filter per lot is confirmed at Eurofins Chicago to be ± 0.0004 g from the provided weight, but other than that, they can be used directly, with the provided tare weights. They must be handled with tongs or forceps. The fliters must be seated with a small amount of DI water.

Alternatively, if filters must be prepared at the lab, follow these steps:

7.3.2.1 Assemble the filtering apparatus. Insert one filter disk into a crucible with the wrinkled side up and place the crucible in a vacuum apparatus. Wet the filter with a small volume of DI water to seat it against the support. Turn on the vacuum and wash with 3 successive ~20 mL volumes of DI water.

7.3.2.2 Continue suction until all traces of water are gone. Turn off the vacuum and place the filter into a crucible. When all filters are prepared, place the rack in a 103-105°C oven for a minimum of 1-hour.

7.3.2.3 After removing the rack from the oven, store it in a desiccator until cooled (a minimum of 30 minutes). The moisture content will equilibrate during cooling.

7.3.2.4 To prepare a filter for VSS, bring the muffle furnace up to 550 ± 50°C. Place the prepared filter and crucible into the preheated muffle furnace for 15-minutes. Remove and allow them to cool to room temperature before putting them into a desiccator. Store them in the desiccator for at least 1-hour prior to use.

7.3.2.5 Weigh the filter and record the weight and crucible number by scanning the sample IDs and electronically entering filter weights directly into an AD batch in TALS through an interface. Always handle the filters with tongs; gloved hands are not acceptable. Standard Methods requires a filter to be dried to a constant tare weight.

7.4 Calibration / Standardization (Daily)

7.4.1 Balance Calibration

Laboratory balances are calibrated and serviced annually by a factory representative. In addition, an analyst checks the balance daily with 3-masses: one in the milligram range and two in the gram range. A record of calibrations and daily checks is kept in the balance module in TALs. Weights calibrated against a Class S set are used by the analysts for daily balance checks.

7.5 Preventive Maintenance

- Clean the balance after each use.
- Verify that the daily calibration check of balance has been performed and is in control prior to use.
- Verify that the daily oven calibration check has been performed and is in control (103-105°C) The temperature is to be recorded when the oven is stable. Corrective action must be performed and recorded in the Daily Oven Temperature Control Log (CHI-22-12-082) when needed.

- The metallic or non-metallic filter support is cleaned by rinsing with DI water on a daily basis. It is also cleaned on a weekly basis by sonicating the metallic port to keep pores from clogging with a 1% acid wash. Replace when needed and document the sonication and replacement on the posted maintenance log sheet.
- Desiccant is inspected daily by the analyst. If the desiccant requires re-drying, place it in a glass beaker and place in the oven overnight. Desiccant changes from a blue hue to a pink hue when drying is necessary. Alternatively, if the desiccator is equipped with a humidity-indicating gauge, that may be used as the indication for the analyst to re-dry the desiccant.
- Change the oil in the vacuum pump monthly or as needed, document oil change on the posted maintenance log sheet.

7.6 Sample Analysis

7.6.1 Set the filter on the filtration apparatus. Turn on the suction and seat the filter if necessary with a small amount of DI water.

7.6.2 Shake the sample vigorously and quantitatively transfer a measured portion to the filter using a graduated cylinder. Work rapidly to prevent settling of the solids in the sample bottle. If less than 20 mL will be analyzed, stir the sample on a stir plate while the sample aliquot is removed by wide-bore pipet from a point midway in the container, halfway between the wall of the container and the vortex.

Note: The wide-bore pipet is not to be used for samples that require compliance with the BP LaMP or TransCanada programs, only Class A glassware is acceptable for use.

7.6.3 Remove all traces of water by continuing to apply the vacuum after the sample has passed through. Maximum filtration time should not exceed 10 minutes. If vacuum surpasses 10 minutes, the analyst will restart process with less volume.

7.6.4 With the suction still on, rinse the graduated cylinder with 10 mL of DI water and add that rinsate to the filter. If a pipet was used, do not rinse it. Maintain vacuum until all the water is drained through. Rinse the filter with a minimum of 2 additional 10 mL portions of DI water, allowing complete drainage between rinses. Apply suction for about 3 minutes after filtration is complete and longer if necessary for the filter to appear dry.

7.6.5 Carefully remove the filter from the suction apparatus and place it back in the aluminum dish or the crucible. Place the dishes or racked crucibles in a 103-105°C oven for 1 hour. Cool in a desiccator and weigh. The Environmental Express Proweigh™ or Whatman™ filters are taken out of the aluminum dishes or crucibles and placed directly on the balance pan to determine the weights. Repeat the drying cycle until a constant weight is obtained (weight loss is <0.0005 g (<0.5 mg) or < 4% of the previous weight, whichever is less.) Record the filtration start and finish times and the times that the samples are put into and taken from the oven.

7.6.6 Repeat the analysis of any sample that yields <0.0025 g (<2.5 mg) of residue if less than 500 mL of sample was used. Use a minimum of 500 mL of sample for the repeat analysis. If insufficient sample volume is available for re-analysis, an NCM must be written to indicate elevated reporting limits for the sample.

7.6.7 If VSS is to be determined, transfer the crucibles and filters from 7.6.3 to a muffle furnace that has been pre-heated to 550 ± 50°C and ignite for 15-20 minutes. Carefully remove the hot dishes and place them on a heat-resistant surface to cool before placing them in a

desiccator. Weigh to the nearest 0.0001 g (0.1 mg). Repeat the cycle of igniting, cooling and weighing until the weight loss is < 4% of the previous weight.

7.7 Documentation

7.7.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

7.7.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

7.7.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs are scanned and attached to the Documents section in the LIMS analytical batch.

7.7.4. Record all sample results and associated QC directly into LIMS. Level I and Level II reviews are performed in LIMS.

Examples of items included in the above reviews are as follows:

- QC data are outside the specified control limits for accuracy and precision
- Unusual detection limit changes are observed
- Samples having unusually high results
- Samples exceeding a known regulatory limit
- Raw data indicating some type of contamination or poor technique
- Inconsistent peak integration (if applicable)
- Transcription errors

8.0 QUALITY CONTROL

8.1 QC Summary

8.1.1 One MB and one LCS will be included in each laboratory lot of 20 or fewer samples. Regardless of the matrix being processed, these standards will be in an aqueous media.

The MB will be examined to determine if contamination is being introduced in the laboratory.

The LCS will be examined to determine accuracy. Accuracy will be measured by the percent recovery (%R) of the LCS. The recovery must be within acceptance limits in order to be considered acceptable (Section 7.1).

8.1.2 One MS/MSD is done per 20 or fewer samples, and one DU is done per 10 or fewer samples, unless a client-specific QAPP specifies otherwise. Results must agree within the appropriate precision/accuracy limits given in Section 7.1 in order to be considered acceptable.

8.2 CORRECTIVE ACTIONS

When an out-of-control situation occurs, the analysts must use his/her best analytical judgment and available resources to determine the corrective action to be taken. The out- of-control situation may be caused by more than one variable. The analyst should seek the assistance of his/her immediate supervisor, QA personnel, or other experienced staff if he/she is uncertain of the cause of the out-of-control situation. The test must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out-of-control situation should be reanalyzed. Out-of-control data must never be released without approval of the Supervisor, Project Manager, Technical Director, QA Manager or the Laboratory Director.

Listed below are steps that must be taken when an out-of-control situation occurs:

- demonstrate that all the problems creating the out of control situation were addressed;
- document the problem and the action which was taken to correct the problem must be documented on the data review checklist; and
- receive approval (signature) of the Supervisor, Project Manager, Technical Director, QA Manager or the Laboratory Director prior to the release of any analytical data associated with the problem.

Suggested Actions to specific out of control situations follow. Frequently there are client-specific QAPP requirements for corrective actions that may supersede the following actions.

Standard	Corrective Actions
LCS	• re-weigh the LCS to verify that an out-of-control situation exists; this refers only to the final weighing, and if the re-reading is within limits, all the remaining QC and sample preparations must be re-read as well. • if the re-weighing of the LCS confirms the contamination or low recovery, determine the source of error, correct the problem and repeat the sample set. (Sources of error include but are not limited to the preparation or shaking of the standard solution, the storage of the diatomaceous earth, an improperly seated or leaky filter, or improper desiccation.) • if the recovery of the LCSs is high, all non-detected sample results may generally be reported, but the out-of-control LCS must be noted in an NCM (non-conformance memo).
MB	• re-weigh the MB to verify contamination at a level > RL (<MDL – Drinking Waters); this refers only to the final weighing step of the analytical process, and if the re-analysis is < RL, all the remaining QC and sample preparations must be re-weighed as well. • if the re-weighing of the blank confirms the contamination, determine the source and correct the problem; • all samples whose concentration is detected at or above the RL but <10 times the MB level must be reprocessed and reanalyzed; any sample which is < RL or >10x MB level need not be reanalyzed. However, the high blank must be noted in an NCM.
DU	• if the sample concentration is <5x RL, then the ± RL rule applies; • the out-of-control DU must be noted on the data review checklist. An NCM should be written to address this issue if required by a specific client and noted in a method note on the backlog, or if the analyst has observed something that would explain the QC failure.
MS	• All matrix spikes must be reported, whether or not they are in control. No NCM is required except when specified by the client and noted in a method

	note on the backlog or if the analyst has observed something that would explain the QC failure.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 Sample Calculation

9.1.1 TSS

$$\frac{\text{mg}}{\text{L}} = \frac{(\text{A} - \text{B}) \times 1{,}000{,}000}{\text{C}}$$

Where:
A = final weight (g) of filter containing sample residue
B = initial weight (g) of filter
C = sample volume (mL)

9.1.2 VSS

$$\frac{\text{mg}}{\text{L}} = \frac{(\text{A} - \text{D}) \times 1{,}000{,}000}{\text{C}}$$

Where:
A = weight of filter and residue before igniting (g)
D = weight of filter and residue after igniting (g)
C = sample volume (mL)

9.2 Accuracy

9.2.1 LCS % Recoveries

$$\frac{\text{observed concentration}}{\text{actual concentration}} \times 100$$

9.2.2 Matrix Spike % Recovery

$$\frac{(\text{spiked sample}) - (\text{unspiked sample})}{\text{spike concentration}} \times 100$$

If other than 100 mL of sample volume was spiked, calculate the spike concentration as follows:

$$\frac{\text{mg}}{\text{L}}\ \text{spike concntration} = \frac{\frac{100\ \text{mg}}{\text{L}} \times 100\ \text{mL}}{\text{mL sample}}$$

9.3 Precision (Matrix Duplicate or Matrix Spike Duplicate)

9.3.1 Matrix Dup. Relative Percent Difference (RPD)

$$RPD = \frac{|\text{orig.sample value} - \text{dup.sample value}|}{\left[\frac{\text{orig.sample value} + \text{dup.sample value}}{2}\right]} \times 100$$

10.0 POLLUTION CONTROL

It is Eurofins policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

10.1 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to UP-WM-001.

The following waste streams are produced when this method is carried out.

- Waste from this procedure will enter the "Non-Regulated" wastestream.

11.0 METHOD PERFORMANCE CRITERIA

Refer to sections 1, 6, 7, and 8.

12.0 REFERENCES

Refer to Section 1.

13.0 ATTACHMENTS

N/A

14.0 REVISION HISTORY

- Revision 26 updated on 08/2/24
- Annual Review
- Section 1.0 added reference to SM 2540 D-2020 and SM 2540 E-2020
- Section 1.1.1 updated corporate SOP
- Section 5.5.3 equation moved to section 9.2.2
- Section 5.5 was re-written
- Section 7.3.2 added requirement to seat pre-weighed filters
- Section 7.7 was re-written
- Section 7.4.1 Balances are recorded in balance calibration module in TALs
- Throughout removed reference to checklist and removed all attachments

Appendix I

Supplemental Water Quality Monitoring Data

I-1 Supplemental Surface Water Quality Information
I-2 Supplemental Groundwater Water Quality Information

I-1

Supplemental Surface Water Quality Information

Appendix Table I.1-1

Stream Flow Summary (Historical)

White Pine Copper LLC

Location: / Date	ARC_01	ARC_02	ARC_03	BDC_01	DKC_01	DKC_02	DKC_03	MLC_01	MLR_01	MLR_02	MLR_03	NTC_01	PLC_01	PNC_01	PNC_02	PNC_03	PNC_04	PRC_01	PRC_02	PRC_03	PTC_01
	Stream Flow (cfs)																				
2/27/05		2.31																			
10/20/14								0.24			26.6	1.98					6.63		11.3		0.31
10/21/14										19.1					3.59	4.69		11.9			
10/22/14	0.27	0.56	2.19	0.13	0.92	4.91	5.61		6.14				0.51	0.42							
4/27/15	0.89		5.61		2.28	5.28	18.8		8.20					1.40			4.89				
4/28/15								0.24			19.2	0.23							8.98		0.12
4/29/15													2.43		8.52	2.63		9.25			
4/30/15		0.24		0.13						9.22											
8/11/15					0.00	-2.74	0.95							-0.05	0.93	0.44	0.18				
8/12/15	0.00	0.00	0.00						0.01			0.00						3.07		2.97	0.00
8/13/15				0.07									0.06								
10/19/15						0.27			0.12					0.00							
10/20/15				0.02			-0.10			30.1			0.20		0.50	0.32	-0.71	1.29			
10/21/15											38.0								1.18		

Prepared by: KRM2

Checked by: MAN

Notes:

1. Data in this table were collected manually. The shading indicates sampling event groupings (sometimes spread over up to two weeks).
2. cfs = cubic feet per second.
3. Blank cells indicate that a flow reading was not attempted/conducted on that date. Flow values shown as '0.00' were measured as such.
4. Negative flow values were recorded at some locations on a few dates. Negative stream flow values can occur due to wind, eddies, or equipment error. While some field forms documented wind as a likely reason for negative flows, most field reports did not provide an
5. Flow data collected on 8/12/15 at MLR-02 & MLR-03 were excluded due to excessively high cfs values, likely due to equipment error. Visual Crossing and Weather Undgerground, two private commercial weather services databases, indicate that Ontonagon, MI did not have a major precipitation event on or around 8/12/15 that would have caused an increased flow event. Also, USGS flow data from the Ontonagon River between 1942-2025 show a median flow of 861 cfs and a mean flow of 1470 cfs; flow on 8/12/15 was between 466 - 480 cfs, indicating low-flow conditions. Links to the flow and precipitation data sources are provided below.

Ontonagon River Near Rockland, MI - USGS Water Data for the Nation

Historical weather data for 49953, Ontonagon, MI, United States

Calumet, MI Weather History | Weather Underground

Table I.1-2
Surface Water Stream Sampling Water Quality
White Pine Copper LLC

	Detected Analytes													
Surface Water Stream Sampling Locations & Date	**Aluminum, Total Recoverable (µg/L)**	**Aluminum, Dissolved (µg/L)**	**Ammonia (mg/L)**	**Bromide (mg/L)**	**Carbon, Dissolved Organic (mg/L)**	**Total Organic Carbon (TOC) (mg/L)**	**Fluoride (mg/L)**	**Nitrate as N (mg/L)**	**Nitrate/Nitrite as N (N) (mg/L)**	**Nitrite as N (mg/L)**	**Sodium, Dissolved (µg/L)**	**Sodium, Total Recoverable (µg/L)**	**Sulfate (mg/L)**	**Sulfide (mg/L)**
ARC-01														
10/22/2014						8.8			0.1				3.5	
2/23/2015						6.6			0.1				4.4	
4/27/2015						7.4			0.1				3.1	
ARC-02														
2/27/2005														
10/22/2014						9.7			0.1				3.6	
3/4/2015						7.8			0.1				4	
4/30/2015						8.5			0.1				3.5	
ARC-03														
10/22/2014						9.7			0.1				3.6	
2/23/2015						7.2			0.1				4.4	
4/27/2015						8.6			0.1				3.3	
BDC-01														
10/22/2014						8.6			0.19				3.2	
4/30/2015						8.7			0.1				3.4	
8/13/2015														
10/20/2015						8.9			0.2				6	
DKC-01														
10/22/2014						8.2			0.1				3.7	
2/23/2015						5.6			0.1				4.5	
4/27/2015						6.5			0.1				3.5	
DKC-02														
10/22/2014						9.9			0.12				4.4	
3/2/2015						7.4			0.18				4.5	
4/27/2015						8.4			0.1				4	
8/11/2015														
10/19/2015						13			0.11				4.3	
DKC-03														
10/22/2014						9.9			0.18				4.6	
3/2/2015						16			0.2				10.2	
4/27/2015						8.6			0.1				3.8	
8/11/2015														
10/20/2015						11			0.2				6	
LKS-01														
10/20/2014						2.8			0.4				3.6	
4/28/2015						3.6			0.33				3	
8/12/2015														
10/26/2015						1.9			0.27				5.5	
LKS-02														
10/20/2014						2.7			0.7				3	
4/28/2015						3.3			0.36				3	
8/12/2015														
11/10/2015						3.4			0.64				16.4	

Table I.1-2 (continued)

Detected Analytes														
Surface Water Stream Sampling Locations & Date	Total Dissolved Solids (mg/L)	Salinity (PSU)	Total Suspended Solids (mg/L)	Alkalinity (mg/L)	Antimony, Dissolved (µg/L)	Antimony, Total Recoverable (µg/L)	Arsenic, Total Recoverable (µg/L)	Arsenic, Dissolved (µg/L)	Barium, Dissolved (µg/L)	Barium, Total Recoverable (µg/L)	Beryllium, Dissolved (µg/L)	Beryllium, Total Recoverable (µg/L)	Bicarbonate Alkalinity (as CaCO3) (mg/L)	Boron, Dissolved (µg/L)
ARC-01														
10/22/2014	70			35		0.25	0.17			13		0.4	35	
2/23/2015	55			45		0.2	1			15		0.4	45	
4/27/2015	57			34		0.4	2			13		0.4	34	
ARC-02														
2/27/2005														
10/22/2014	88			42		0.25	0.17			20		0.4	42	
3/4/2015	61			60		0.3	1			26		0.4	60	
4/30/2015	71			45		0.4	2			19		0.4	45	
ARC-03														
10/22/2014	83			38		0.25	0.17			32		0.4	38	
2/23/2015	85			60		0.2	1			46		0.4	60	
4/27/2015	67			39		0.4	2			27		0.4	39	
BDC-01														
10/22/2014	99			66		0.25	0.44			22		0.4	66	
4/30/2015	73			52		0.4	2			16		0.4	52	
8/13/2015						10	1.9			36		2		
10/20/2015	100			86		10	10			32		2	86	
DKC-01														
10/22/2014	91			44		0.25	0.17			28		0.4	44	
2/23/2015	84			67		0.2	1			37		0.4	67	
4/27/2015	48			36		0.4	2			24		0.4	36	
DKC-02														
10/22/2014	78			33		0.25	0.21			26		0.4	33	
3/2/2015	71			61		0.3	1			35		0.4	61	
4/27/2015	56			29		0.4	2			21		0.4	29	
8/11/2015						10	10			45		2		
10/19/2015	130			96		10	10			55		2	96	
DKC-03														
10/22/2014	81			34		0.25	0.17			27		0.4	34	
3/2/2015	136			54		0.6	2			67		0.8	108	
4/27/2015	49			31		0.4	2			23		0.4	31	
8/11/2015						10	10			41		2		
10/20/2015	87			64		10	10			47		2	64	
LKS-01														
10/20/2014	69			42		0.25	0.17			26		0.4	42	
4/28/2015	51			39		0.4	2			17		0.4	39	
8/12/2015						10	10			15		2		
10/26/2015	56			48		10	10			13		2	48	
LKS-02														
10/20/2014	59			42		0.25	0.17			13		0.4	42	
4/28/2015	49			42		0.4	2			14		0.4	42	
8/12/2015														
11/10/2015	102			40		2	20			22		4	86	

Table I.1-2 (continued)

Surface Water Stream Sampling Locations & Date	Boron, Total Recoverable (µg/L)	Cadmium, Dissolved (µg/L)	Cadmium, Total Recoverable (µg/L)	Calcium, Dissolved (µg/L)	Calcium, Total Recoverable (µg/L)	Carbonate Alkalinity as CaCO3 (mg/L)	Total Chloride (mg/L)	Chromium, Dissolved (µg/L)	Chromium, Total Recoverable (µg/L)	Cobalt, Dissolved (µg/L)	Cobalt, Total Recoverable (µg/L)	Copper, Dissolved (µg/L)	Total Copper (µg/L)	Cyanide, Total (mg/L)
	Detected Analytes													
ARC-01														
10/22/2014	30		0.1			35	3		0.8		4		12	
2/23/2015	40		0.1			45	4		2.9		3		9.1	
4/27/2015	40		0.1			34	4		3.4		1		6.7	
ARC-02														
2/27/2005														
10/22/2014	30		0.1			42	3		0.8		4		14	
3/4/2015	40		0.1			60	3		4.8		2		12	
4/30/2015	40		0.1			45	4		3.9		2		10	
ARC-03														
10/22/2014	30		0.1			38	4		0.8		4		12	
2/23/2015	40		0.1			60	10		3.6		3		8	
4/27/2015	40		0.1			39	4		3.8		1		8.6	
BDC-01														
10/22/2014	30		0.1				3		0.8		4		50	
4/30/2015	40		0.1				4		3.7		2		49	
8/13/2015	100		1						5		20		19	
10/20/2015	100		3				8		4.6		10		20	
DKC-01														
10/22/2014	30		0.1			44	3		0.8		4		0.0081	
2/23/2015	40		0.1			67	3		4.8		3		0.0064	
4/27/2015	40		0.1			36	4		6.8		1		0.0066	
DKC-02														
10/22/2014	30		0.1			33	3		0.8		4		13	
3/2/2015	40		0.1			61	7		4.4		2		8.4	
4/27/2015	40		0.1			29	9		8.2		1		11	
8/11/2015	100		1						4.4		20		10	
10/19/2015	100		3			96	20		5.3		10		6.6	
DKC-03														
10/22/2014	30		0.1			34	3		0.8		4		13	
3/2/2015	80		0.2			54	3		7.8		4		9.5	
4/27/2015	40		0.1			31	4		16		1		9.8	
8/11/2015	100		1						3.9		20		10	
10/20/2015	100		3			64	20		4.2		10		4.9	
LKS-01														
10/20/2014	30		0.1			42	3		1.1		4		6.9	
4/28/2015	40		0.1			39	4		4.6		1		5	
8/12/2015	100		1						3.7		20		10	
10/26/2015	100		1			48	5		3.1		10		3.1	
LKS-02														
10/20/2014	40		0.1			42	3		0.8		4		5.2	
4/28/2015	40		0.1			42	4		6		2.7		5.5	
8/12/2015													10	
11/10/2015	240		2			42	4		6.5		20		2.4	

Table I.1-2 (continued)

Surface Water Stream Sampling Locations & Date	Hardness (mg/L)	Total Iron (µg/L)	Iron, Dissolved (µg/L)	Lead, Dissolved (µg/L)	Lead, Total Recoverable (µg/L)	Lithium, Dissolved (µg/L)	Lithium, Total Recoverable (µg/L)	Manganese, Dissolved (µg/L)	Manganese, Total Recoverable (µg/L)	Magnesium, Dissolved (µg/L)	Magnesium, Total Recoverable (µg/L)	Dissolved Mercury (ng/L)	Mercury, Total Recoverable (ng/L)	Methyl Mercury, Dissolved (ng/L)
	Detected Analytes													
ARC-01														
10/22/2014	38	340			10		6		8.6				120	
2/23/2015	45	430			0.1		6		30				120	
4/27/2015	32	270			0.1		6		17				120	
ARC-02														
2/27/2005														
10/22/2014	45	390			10		6		2.5				120	
3/4/2015	61	1200			0.17		6		100				120	
4/30/2015	41	450			0.1		6		46				120	
ARC-03														
10/22/2014	43	350			10		6		0.5				120	
2/23/2015	62	420			0.1		6		15				120	
4/27/2015	37	280			0.1		6		12				120	
BDC-01														
10/22/2014	66	1000			10		6		91				120	
4/30/2015	45	820			0.1		6		95				120	
8/13/2015	81	1600			10		30		480					
10/20/2015	74	670			3		30		190				200	
DKC-01														
10/22/2014	48	380			10		6		0.5				120	
2/23/2015	69	340			0.1		6		24				120	
4/27/2015	35	350			0.11		6		16				120	
DKC-02														
10/22/2014	36	640			10		6		4.3				120	
3/2/2015	58	1100			0.1		6		24				120	
4/27/2015	28	480			0.13		6		19				120	
8/11/2015	65	760			10		30		140					
10/19/2015	87	800			3		6.2		220				200	
DKC-03														
10/22/2014	37	650			10		6		5.4				120	
3/2/2015	56	1400			0.2		12		49				120	
4/27/2015	28	490			0.11		6		19				120	
8/11/2015	58	160			10		30		28					
10/20/2015	55	240			3		30		39				200	
LKS-01														
10/20/2014	52	2000			10		6		29				120	
4/28/2015	41	320			0.12		6		14				120	
8/12/2015	48	550			10		30		23					
10/26/2015	47	89			3		30		2.4				200	
LKS-02														
10/20/2014	48	240			10		6		7.5				120	
4/28/2015	41	170			0.1		6		11				120	
8/12/2015	46	590												
11/10/2015	46	26			6		60		18				200	

Table I.1-2 (continued)

		Detected Analytes												
Surface Water Stream Sampling Locations & Date	**Methyl Mercury, Total Recoverable (ng/L)**	**Molybdenum, Dissolved (µg/L)**	**Molybdenum, Total Recoverable (µg/L)**	**Nickel, Dissolved (µg/L)**	**Nickel, Total Recoverable (µg/L)**	**Phosphorus-Total (as P) (mg/L)**	**Potassium, Dissolved (µg/L)**	**Potassium, Total Recoverable (µg/L)**	**Selenium, Dissolved (µg/L)**	**Selenium, Total Recoverable (µg/L)**	**Silver, Dissolved (µg/L)**	**Silver, Total Recoverable (µg/L)**	**Strontium, Dissolved (µg/L)**	**Strontium, Total Recoverable (µg/L)**
ARC-01														
10/22/2014					8					1.4		12		31
2/23/2015					10					1		2.5		32
4/27/2015					10					1		0.3		29
ARC-02														
2/27/2005														
10/22/2014					8					1.4		12		51
3/4/2015					10					1		2		71
4/30/2015					10					1		0.3		50
ARC-03														
10/22/2014					8					1.4		12		59
2/23/2015					10					1		2		93
4/27/2015					10					1		0.3		53
BDC-01														
10/22/2014					8					1.4		12		61
4/30/2015					10					1		0.3		41
8/13/2015					30					10		10		80
10/20/2015					30					20		10		78
DKC-01														
10/22/2014					8					1.4		12		35
2/23/2015					10					1		3.4		47
4/27/2015					10					1		0.3		28
DKC-02														
10/22/2014					8					1.4		12		39
3/2/2015					10					1		2		65
4/27/2015					10					1		0.3		31
8/11/2015					30					10		11		81
10/19/2015					30					20		10		120
DKC-03														
10/22/2014					8					1.4		12		41
3/2/2015					20					2		4		124
4/27/2015					10					1		0.3		32
8/11/2015					30					10		10		74
10/20/2015					30					20		10		83
LKS-01														
10/20/2014					8.4					1.4		12		32
4/28/2015					10					1		0.3		29
8/12/2015					30					10		10		23
10/26/2015					30					10		10		26
LKS-02														
10/20/2014					8					1.4		12		26
4/28/2015					10					1		0.3		28
8/12/2015														
11/10/2015					60					20		2		45

Table I.1-2 (continued)

		Detected Analytes								
Surface Water Stream Sampling Locations & Date	**Thallium, Dissolved (µg/L)**	**Thallium, Total Recoverable (µg/L)**	**Tin, Dissolved (µg/L)**	**Tin, Total Recoverable (µg/L)**	**Uranium, Dissolved (µg/L)**	**Uranium, Total Recoverable (µg/L)**	**Vanadium, Dissolved (µg/L)**	**Vanadium Total Recoverable (µg/L)**	**Zinc, Dissolved (µg/L)**	**Zinc, Total Recoverable (µg/L)**
ARC-01										
10/22/2014		0.3				0.23		0.39		10
2/23/2015		0.1				0.23		1.1		10
4/27/2015		0.1				0.13		1.1		10
ARC-02										
2/27/2005										
10/22/2014		0.3				0.31		0.41		10
3/4/2015		0.1				0.31		1.5		15
4/30/2015		0.1				0.167		1.4		10
ARC-03										
10/22/2014		0.3				0.23		0.73		10
2/23/2015		0.1				0.59		1.1		10
4/27/2015		0.1				0.226		1.4		10
BDC-01										
10/22/2014		0.3				0.23		0.3		10
4/30/2015		0.1				0.129		0.84		10
8/13/2015		1				0.064		10		30
10/20/2015		1				0.018		4.4		30
DKC-01										
10/22/2014		0.3				0.23		0.95		10
2/23/2015		0.1				0.51		1.4		10
4/27/2015		0.1				0.148		1.7		10
DKC-02										
10/22/2014		0.3				0.23		0.94		10
3/2/2015		0.1				0.93		1.3		15
4/27/2015		0.1				0.266		1.8		10
8/11/2015		1				0.85		10		30
10/19/2015		1				0.5		1.4		30
DKC-03										
10/22/2014		0.3				0.23		0.82		10
3/2/2015		0.2				1.19		1.5		30
4/27/2015		0.1				0.226		1.7		10
8/11/2015		1				0.41		10		30
10/20/2015		1				0.079		0.88		30
LKS-01										
10/20/2014		0.3				0.23		3.5		10
4/28/2015		0.1				0.129		1.9		10
8/12/2015		1				0.16		1.3		30
10/26/2015		1				0.14		0.92		30
LKS-02										
10/20/2014		0.3				0.23		0.54		10
4/28/2015		0.1				0.131		1.4		10
8/12/2015								2.1		
11/10/2015		2				0.24		0.73		150

Table I.1-2 (continued)

Surface Water Stream Sampling Locations & Date	Detected Analytes													
	Aluminum, Total Recoverable (µg/L)	Aluminum, Dissolved (µg/L)	Ammonia (mg/L)	Bromide (mg/L)	Carbon, Dissolved Organic (mg/L)	Total Organic Carbon (TOC) (mg/L)	Fluoride (mg/L)	Nitrate as N (mg/L)	Nitrate/Nitrite as N (N) (mg/L)	Nitrite as N (mg/L)	Sodium, Dissolved (µg/L)	Sodium, Total Recoverable (µg/L)	Sulfate (mg/L)	Sulfide (mg/L)
MLC-01														
10/20/2014						9.6			0.14				3.1	
4/28/2015						8.2			0.1				3	
MLR-01														
10/22/2014						23			0.2				14.6	
2/23/2015						7.5			0.1				7.3	
4/27/2015						8.4			0.1				5.1	
8/12/2015														
10/19/2015						46			0.4				10.8	
MLR-02														
10/21/2014						14			0.24				6.7	
3/5/2015						3.6			0.35				3	
4/30/2015						8.6			0.12				4.7	
8/12/2015														
10/20/2015						3.6			0.12				6	
MLR-03														
10/20/2014						14			0.1				7.1	
3/5/2015						7.3			0.69				6	
4/28/2015						9.4			0.1				4.8	
8/12/2015														
10/21/2015						6.4			0.2				6	
NTC-01														
10/20/2014						7.6			2.8				26	
2/27/2015						8.4			0.1				6.5	
4/28/2015						9.1			0.12				3.2	
PLC-01														
10/22/2014						11			0.12				3	
2/24/2015						9.4			0.1				5.2	
4/29/2015						19.5			0.2				7.2	
8/13/2015														
10/20/2015						10			0.2				6	
PNC-01														
10/22/2014						10			0.1				4.3	
2/23/2015						8.9			0.1				7.5	
4/27/2015						18			0.2				7.7	
8/11/2015														
10/19/2015						13			1.9				3.9	
PNC-02														
10/21/2014						10			0.1				3.6	
2/25/2015						9.8			0.1				7.1	
4/29/2015						9			0.1				3.5	
8/11/2015														
10/20/2015						11			0.2				6	

Table I.1-2 (continued)

Detected Analytes														
Surface Water Stream Sampling Locations & Date	Total Dissolved Solids (mg/L)	Salinity (PSU)	Total Suspended Solids (mg/L)	Alkalinity (mg/L)	Antimony, Dissolved (µg/L)	Antimony, Total Recoverable (µg/L)	Arsenic, Total Recoverable (µg/L)	Arsenic, Dissolved (µg/L)	Barium, Dissolved (µg/L)	Barium, Total Recoverable (µg/L)	Beryllium, Dissolved (µg/L)	Beryllium, Total Recoverable (µg/L)	Bicarbonate Alkalinity (as CaCO3) (mg/L)	Boron, Dissolved (µg/L)
MLC-01														
10/20/2014	140			55		0.25	0.17			60		0.4	55	
4/28/2015	97			49		0.4	2			47		0.4	49	
MLR-01														
10/22/2014	183			26		0.5	0.34			43		0.8	52	
2/23/2015	68			47		0.2	1			21		0.4	47	
4/27/2015	54			22		0.4	2			18		0.4	22	
8/12/2015						10	10			41		2		
10/19/2015	290			95		20	20			89		4	192	
MLR-02														
10/21/2014	110			43		0.25	0.29			27		0.4	43	
3/5/2015	51			51		0.3	1			17		0.4	51	
4/30/2015	83			42		0.4	2			20		0.4	42	
8/12/2015						10	10			14		2		
10/20/2015	73			56		10	10			16		2	56	
MLR-03														
10/20/2014	100			37		0.25	0.17			28		0.4	37	
3/5/2015	113			52		0.6	2			37		0.8	105	
4/28/2015	72			36		0.4	2			22		0.4	36	
8/12/2015						20	20			29		4		
10/21/2015	120			89		10	10			18		2	89	
NTC-01														
10/20/2014	370			80		0.25	0.21			120		0.4	80	
2/27/2015	200			110		0.2	1			86		0.4	110	
4/28/2015	82			52		0.4	2			37		0.4	52	
PLC-01														
10/22/2014	130			90		0.25	0.23			25		0.4	90	
2/24/2015	150			120		0.2	1			43		0.4	120	
4/29/2015	250			86		0.8	4			54		0.8	173	
8/13/2015						10	5.6			300		2		
10/20/2015	180			160		10	10			46		2	160	
PNC-01														
10/22/2014	76			26		0.25	0.17			13		0.4	26	
2/23/2015	62			29		0.2	1			12		0.4	29	
4/27/2015	85			1		0.8	4			18.9		0.8	41	
8/11/2015						10	10			48		2		
10/19/2015	130			100		10	10			33		2	100	
PNC-02														
10/21/2014	94			58		0.25	0.17			32		0.4	58	
2/25/2015	150			110		0.2	1			79		0.4	110	
4/29/2015	98			58		0.4	2			31		0.4	58	
8/11/2015														
10/20/2015	230			170		10	10			110		2	170	

Table I.1-2 (continued)

Surface Water Stream Sampling Locations & Date	Boron, Total Recoverable (µg/L)	Cadmium, Dissolved (µg/L)	Cadmium, Total Recoverable (µg/L)	Calcium, Dissolved (µg/L)	Calcium, Total Recoverable (µg/L)	Carbonate Alkalinity as CaCO3 (mg/L)	Total Chloride (mg/L)	Chromium, Dissolved (µg/L)	Chromium, Total Recoverable (µg/L)	Cobalt, Dissolved (µg/L)	Cobalt, Total Recoverable (µg/L)	Copper, Dissolved (µg/L)	Total Copper (µg/L)	Cyanide, Total (mg/L)
	Detected Analytes													
MLC-01														
10/20/2014	30		0.1			55	19		0.8		4		12	
4/28/2015	40		0.1			49	11		6		1.4		12	
MLR-01														
10/22/2014	60		0.2			26	3		1.72		8		15	
2/23/2015	40		0.1			47	12		4.4		3		9.6	
4/27/2015	40		0.1			22	11		5.6		1		9.4	
8/12/2015	100		1						5.3		20		3.8	
10/19/2015	200		6			95	20		11.5		20		9.1	
MLR-02														
10/21/2014	48		0.1			43	6		0.8		4		51	
3/5/2015	40		0.1			51	3		4		2		16	
4/30/2015	40		0.1			42	4		4.7		2		33	
8/12/2015	100		1						3.3		20		4.9	
10/20/2015	100		3			56	10		3.8		10		13	
MLR-03														
10/20/2014	30		0.1			37	8		0.9		4		50	
3/5/2015	80		0.2			52	3		7.7		4		19	
4/28/2015	40		0.1			36	5		5.1		1		36	
8/12/2015	200		2						7		40		6.3	
10/21/2015	100		3			89	11		5.1		10		14	
NTC-01														
10/20/2014	150		0.1			80	120		0.8		4		8.7	
2/27/2015	67		0.1			110	50		9.6		3		11	
4/28/2015	40		0.1			52	11		4.7		1		10	
PLC-01														
10/22/2014	30		0.1			90	3		0.8		4		46	
2/24/2015	40		0.1			120	3		7.3		3		55	
4/29/2015	80		0.2			86	7		12.9		4		58	
8/13/2015	100		0.22						15		20		69	
10/20/2015	100		3			160	7		8.3		10		21	
PNC-01														
10/22/2014	30		0.1			26	3		0.8		4		16	
2/23/2015	40		0.1			29	3		2.6		3		12	
4/27/2015	80		0.2			22	7		6.1		2		12	
8/11/2015	100		0.11						6.2		20		3.6	
10/19/2015	100		3			100	20		5.1		10		6.4	
PNC-02														
10/21/2014	40		0.1			58	5		0.8		4		15	
2/25/2015	40		0.1			110	9		7.2		3		17	
4/29/2015	40		0.1			58	8		15		1		18	
8/11/2015													6	
10/20/2015	100		3			170	20		11		10		14	

Table I.1-2 (continued)

Surface Water Stream Sampling Locations & Date	Hardness (mg/L)	Total Iron (µg/L)	Iron, Dissolved (µg/L)	Lead, Dissolved (µg/L)	Lead, Total Recoverable (µg/L)	Lithium, Dissolved (µg/L)	Lithium, Total Recoverable (µg/L)	Manganese, Dissolved (µg/L)	Manganese, Total Recoverable (µg/L)	Magnesium, Dissolved (µg/L)	Magnesium, Total Recoverable (µg/L)	Dissolved Mercury (ng/L)	Mercury, Total Recoverable (ng/L)	Methyl Mercury, Dissolved (ng/L)
					Detected Analytes									
MLC-01														
10/20/2014	80	190			10		6		2.5				120	
4/28/2015	55	170			0.1		6		30				120	
MLR-01														
10/22/2014	34	1000			20		12		20				120	
2/23/2015	50	1300			0.33		6		26				120	
4/27/2015	25	870			0.26		6		27				120	
8/12/2015	84	600			10		30		78					
10/19/2015	91	560			6		37.1		210				200	
MLR-02														
10/21/2014	51	1100			10		6		19				120	
3/5/2015	55	290			0.1		6		23				120	
4/30/2015	44	620			0.18		6		28				120	
8/12/2015	50	130			10		30		18					
10/20/2015	53	72			3		30		21				200	
MLR-03														
10/20/2014	45	1200			10		6		10				120	
3/5/2015	55	350			0.2		12		44				120	
4/28/2015	41	760			0.24		6		26				120	
8/12/2015	51	84			20		60		30					
10/21/2015	86	58			3		30		65				200	
NTC-01														
10/20/2014	180	190			10		6		18				120	
2/27/2015	140	2600			0.1		7.4		730				120	
4/28/2015	57	490			0.1		6		62				120	
PLC-01														
10/22/2014	96	1900			10		6		1.4				120	
2/24/2015	120	1100			0.1		6		260				120	
4/29/2015	78	450			0.2		12		124				120	
8/13/2015	170	11000			10		30		14000					
10/20/2015	150	780			3		15		320				200	
PNC-01														
10/22/2014	30	830			10		6		42				120	
2/23/2015	32	1800			0.11		6		77				120	
4/27/2015	19	500			560.1		6.1		42.4				120	
8/11/2015	95	5100			10		30		3900					
10/19/2015	95	4200			3		30		560				200	
PNC-02														
10/21/2014	66	440			10		6		25				120	
2/25/2015	110	2500			0.1		6		1500				120	
4/29/2015	59	530			0.1		6		59				120	
8/11/2015	160	290												
10/20/2015	180	330			3		12		250				200	

Table I.1-2 (continued)

Surface Water Stream Sampling Locations & Date	Methyl Mercury, Total Recoverable (ng/L)	Detected Analytes												
		Molybdenum, Dissolved (µg/L)	Molybdenum, Total Recoverable (µg/L)	Nickel, Dissolved (µg/L)	Nickel, Total Recoverable (µg/L)	Phosphorus-Total (as P) (mg/L)	Potassium, Dissolved (µg/L)	Potassium, Total Recoverable (µg/L)	Selenium, Dissolved (µg/L)	Selenium, Total Recoverable (µg/L)	Silver, Dissolved (µg/L)	Silver, Total Recoverable (µg/L)	Strontium, Dissolved (µg/L)	Strontium, Total Recoverable (µg/L)
MLC-01														
10/20/2014					8					1.4		12		130
4/28/2015					10					1		0.3		99
MLR-01														
10/22/2014					16					2.8		24		62
2/23/2015					10					1		2		39
4/27/2015					10					1		0.3		24
8/12/2015					30					10		10		88
10/19/2015					60					40		15		177
MLR-02														
10/21/2014					11					1.4		12		38
3/5/2015					10					1		2.7		33
4/30/2015					10					1		0.3		36
8/12/2015					30					10		10		25
10/20/2015					30					20		10		30
MLR-03														
10/20/2014					8					1.4		12		38
3/5/2015					20					2		5.4		68
4/28/2015					10					1		0.3		33
8/12/2015					60					20		20		54
10/21/2015					30					20		2		58
NTC-01														
10/20/2014					11					1.4		12		430
2/27/2015					10					1		4.1		260
4/28/2015					10					1		0.3		110
PLC-01														
10/22/2014					8					1.4		12		68
2/24/2015					10					1		5		91
4/29/2015					20					2		0.6		123
8/13/2015					30					10		10		140
10/20/2015					30					20		10		110
PNC-01														
10/22/2014					8					1.4		12		25
2/23/2015					10					1		2		24
4/27/2015					15.9					1.003		10.3		19
8/11/2015					30					10		10		71
10/19/2015					30					20		10		69
PNC-02														
10/21/2014					8					1.4		12		81
2/25/2015					10					1		5.7		150
4/29/2015					10					1		0.3		73
8/11/2015														
10/20/2015					30					20		2.1		330

Table I.1-2 (continued)

		Detected Analytes								
Surface Water Stream Sampling Locations & Date	**Thallium, Dissolved (µg/L)**	**Thallium, Total Recoverable (µg/L)**	**Tin, Dissolved (µg/L)**	**Tin, Total Recoverable (µg/L)**	**Uranium, Dissolved (µg/L)**	**Uranium, Total Recoverable (µg/L)**	**Vanadium, Dissolved (µg/L)**	**Vanadium Total Recoverable (µg/L)**	**Zinc, Dissolved (µg/L)**	**Zinc, Total Recoverable (µg/L)**
MLC-01										
10/20/2014		0.3				0.29		0.3		10
4/28/2015		0.1				0.252		1.2		10
MLR-01										
10/22/2014		0.6				0.46		1.8		20
2/23/2015		0.1				0.23		2.2		10
4/27/2015		0.1				0.129		2.5		10
8/12/2015		0.58				1.7		10		30
10/19/2015		2				0.89		1.1		60
MLR-02										
10/21/2014		0.3				0.23		1.9		10
3/5/2015		0.1				0.23		0.81		15
4/30/2015		0.1				0.15		1.8		10
8/12/2015		1				0.15		10		30
10/20/2015		1				0.07		1.5		30
MLR-03										
10/20/2014		0.3				0.23		1.9		10
3/5/2015		0.2				0.46		0.82		30
4/28/2015		0.1				0.16		2.4		10
8/12/2015		1.57				0.33		10		60
10/21/2015		1				0.21		0.85		30
NTC-01										
10/20/2014		0.3				0.24		0.3		10
2/27/2015		0.1				0.28		1.6		10
4/28/2015		0.1				0.13		1.7		10
PLC-01										
10/22/2014		0.3				0.23		0.3		10
2/24/2015		0.1				0.24		0.78		11
4/29/2015		0.2				0.545		0.93		20
8/13/2015		1				0.34		3.3		12
10/20/2015		1				0.13		1.7		30
PNC-01										
10/22/2014		0.3				0.23		0.45		10
2/23/2015		0.1				0.23		1.2		10
4/27/2015		0.4				17.129		0.1		10.129
8/11/2015		1				0.24		10		30
10/19/2015		1				0.041		0.64		30
PNC-02										
10/21/2014		0.3				0.23		0.38		10
2/25/2015		0.1				0.28		0.97		10
4/29/2015		0.1				0.164		1.3		10
8/11/2015								10		
10/20/2015		1				0.24		0.52		30

Table I.1-2 (continued)

Surface Water Stream Sampling Locations & Date	Detected Analytes													
	Aluminum, Total Recoverable (µg/L)	Aluminum, Dissolved (µg/L)	Ammonia (mg/L)	Bromide (mg/L)	Carbon, Dissolved Organic (mg/L)	Total Organic Carbon (TOC) (mg/L)	Fluoride (mg/L)	Nitrate as N (mg/L)	Nitrate/Nitrite as N (N) (mg/L)	Nitrite as N (mg/L)	Sodium, Dissolved (µg/L)	Sodium, Total Recoverable (µg/L)	Sulfate (mg/L)	Sulfide (mg/L)
PNC-03														
10/21/2014						11			0.1				3.6	
3/4/2015						18.7			0.2				9.1	
4/29/2015						9.5			0.12				3.5	
8/11/2015														
10/20/2015						12			0.2				6	
PNC-04														
10/20/2014						22			0.6				7.1	
3/2/2015						8.7			0.12				4.6	
4/27/2015						9.2			0.1				3.6	
8/11/2015														
10/20/2015						13			0.24				6	
PRC-01														
10/21/2014						10.7			0.37				90	
2/26/2015						11			0.22				116	
4/29/2015						4.2			0.1				42	
8/12/2015														
10/20/2015						5.3			0.2				54	
PRC-02														
10/20/2014						5.4			0.1				45	
3/5/2015						5.6			0.1				58	
4/28/2015						4.4			0.1				40	
10/21/2015						6.4			0.2				51	
PRC-03														
8/12/2015														
PTC-01														
10/20/2014						7.9			0.23				3	
2/24/2015						4.7			0.1				3.2	
4/28/2015						6.7			0.1				3	

Table I.1-2 (continued)

Detected Analytes														
Surface Water Stream Sampling Locations & Date	Total Dissolved Solids (mg/L)	Salinity (PSU)	Total Suspended Solids (mg/L)	Alkalinity (mg/L)	Antimony, Dissolved (µg/L)	Antimony, Total Recoverable (µg/L)	Arsenic, Total Recoverable (µg/L)	Arsenic, Dissolved (µg/L)	Barium, Dissolved (µg/L)	Barium, Total Recoverable (µg/L)	Beryllium, Dissolved (µg/L)	Beryllium, Total Recoverable (µg/L)	Bicarbonate Alkalinity (as CaCO3) (mg/L)	Boron, Dissolved (µg/L)
PNC-03														
10/21/2014	120			66		0.25	0.17			37		0.4	66	
3/4/2015	350			110		0.6	2			152		0.8	220	
4/29/2015	110			58		0.4	2			37		0.4	58	
8/11/2015						10	10			98		2		
10/20/2015	290			150		10	10			110		2	150	
PNC-04														
10/20/2014	240			60		0.5	0.34			74		0.8	122	
3/2/2015	170			100		0.3	1			64		0.4	100	
4/27/2015	89			50		0.4	2			32		0.4	50	
8/11/2015						10	10			87		2		
10/20/2015	250			130		10	10			82		2	130	
PRC-01														
10/21/2014	1190			100		0.67	1.38			260		0.8	198	
2/26/2015	1330			160		0.74	2			410		0.8	330	
4/29/2015	570			98		0.4	2			94		0.4	98	
8/12/2015						10	10			180		2		
10/20/2015	860			93		10	10			230		2	93	
PRC-02														
10/20/2014	580			98		0.45	0.72			140		0.4	98	
3/5/2015	680			170		0.37	1			210		0.4	170	
4/28/2015	510			97		0.4	2			100		0.4	97	
10/21/2015	850			98		10	10			230		2	98	
PRC-03														
8/12/2015						10	10			170		2		
PTC-01														
10/20/2014	130			80		0.25	0.17			92		0.4	80	
2/24/2015	150			81		0.2	1			100		0.4	81	
4/28/2015	92			60		0.4	2			59		0.4	60	

Table I.1-2 (continued)

Surface Water Stream Sampling Locations & Date	Boron, Total Recoverable (µg/L)	Cadmium, Dissolved (µg/L)	Cadmium, Total Recoverable (µg/L)	Calcium, Dissolved (µg/L)	Calcium, Total Recoverable (µg/L)	Carbonate Alkalinity as CaCO3 (mg/L)	Total Chloride (mg/L)	Chromium, Dissolved (µg/L)	Chromium, Total Recoverable (µg/L)	Cobalt, Dissolved (µg/L)	Cobalt, Total Recoverable (µg/L)	Copper, Dissolved (µg/L)	Total Copper (µg/L)	Cyanide, Total (mg/L)
	Detected Analytes													
PNC-03														
10/21/2014	41		0.1			66	9		0.8		4		16	
3/4/2015	80		0.2			110	23		17.9		4.1		20	
4/29/2015	40		0.1			58	9		6		1.1		18	
8/11/2015	100		1						13		20		8.8	
10/20/2015	100		3			150	72		13		10		14	
PNC-04														
10/20/2014	81		0.2			60	10		1.6		8		14	
3/2/2015	40		0.1			100	27		8.8		2		15	
4/27/2015	40		0.1			50	11		4.7		1		16	
8/11/2015	100		1						11		20		6.7	
10/20/2015	100		3			130	55		11		10		12	
PRC-01														
10/21/2014	740		0.2			100	190		1.6		8		41	
2/26/2015	480		0.2			160	240		54		6		58	
4/29/2015	150		0.1			98	170		16		2.8		46	
8/12/2015	410		1						24		20		10	
10/20/2015	550		3			93	330		29		10		16	
PRC-02														
10/20/2014	360		0.1			98	190		0.8		4		36	
3/5/2015	230		0.1			170	240		28		2		51	
4/28/2015	150		0.1			97	170		18		1		48	
10/21/2015	490		3			98	340		29		3.3		20	
PRC-03														
8/12/2015	390		1						23		20		12	
PTC-01														
10/20/2014	44		0.1			80	15		0.8		4		5.7	
2/24/2015	40		0.1			81	21		6.9		3		9.3	
4/28/2015	40		0.1			60	8		4.7		1		7.6	

Table I.1-2 (continued)

Surface Water Stream Sampling Locations & Date	Hardness (mg/L)	Total Iron (µg/L)	Iron, Dissolved (µg/L)	Lead, Dissolved (µg/L)	Lead, Total Recoverable (µg/L)	Lithium, Dissolved (µg/L)	Lithium, Total Recoverable (µg/L)	Manganese, Dissolved (µg/L)	Manganese, Total Recoverable (µg/L)	Magnesium, Dissolved (µg/L)	Magnesium, Total Recoverable (µg/L)	Dissolved Mercury (ng/L)	Mercury, Total Recoverable (ng/L)	Methyl Mercury, Dissolved (ng/L)
	Detected Analytes													
PNC-03														
10/21/2014	74	450			10		6		54				120	
3/4/2015	140	1900			0.42		13		920				120	
4/29/2015	65	520			0.1		6		92				120	
8/11/2015	200	260			10		11		170					
10/20/2015	230	270			3		17		81				200	
PNC-04														
10/20/2014	73	400			20		12		40				120	
3/2/2015	150	1400			0.1		6		140				120	
4/27/2015	55	460			0.1		6		46				120	
8/11/2015	170	280			10		16		150					
10/20/2015	170	210			3		15		69				200	
PRC-01														
10/21/2014	250	280			20		32		81				120	
2/26/2015	400	110			0.2		138		490				120	
4/29/2015	200	450			0.1		34		73				120	
8/12/2015	300	51			10		62		73					
10/20/2015	350	84			3		72		25				200	
PRC-02														
10/20/2014	250	260			10		20		46				120	
3/5/2015	390	210			0.1		60		160				120	
4/28/2015	210	570			0.1		34		65				120	
10/21/2015	350	370			3		63		120				120	
PRC-03														
8/12/2015	300	370			10		56		160					
PTC-01														
10/20/2014	93	80			10		6		0.5					
2/24/2015	100	40			0.1		6		23					
4/28/2015	60	110			0.48		6		17					

Table I.1-2 (continued)

		Detected Analytes												
Surface Water Stream Sampling Locations & Date	Methyl Mercury, Total Recoverable (ng/L)	Molybdenum, Dissolved (µg/L)	Molybdenum, Total Recoverable (µg/L)	Nickel, Dissolved (µg/L)	Nickel, Total Recoverable (µg/L)	Phosphorus-Total (as P) (mg/L)	Potassium, Dissolved (µg/L)	Potassium, Total Recoverable (µg/L)	Selenium, Dissolved (µg/L)	Selenium, Total Recoverable (µg/L)	Silver, Dissolved (µg/L)	Silver, Total Recoverable (µg/L)	Strontium, Dissolved (µg/L)	Strontium, Total Recoverable (µg/L)
PNC-03														
10/21/2014					8					1.4		12		110
3/4/2015					20					2.1		8.4		450
4/29/2015					10					1		0.3		110
8/11/2015					30					10		10		440
10/20/2015					30					20		10		510
PNC-04														
10/20/2014					16					2.8		24		240
3/2/2015					10					1		6.4		250
4/27/2015					10					1		0.3		96
8/11/2015					30					10		10		510
10/20/2015					30					20		10		520
PRC-01														
10/21/2014					48					2.8		24		1810
2/26/2015					20					4.9		31		2500
4/29/2015					10					1.2		0.3		780
8/12/2015					30					10		10		1300
10/20/2015					30					2.5		10		1400
PRC-02														
10/20/2014					17					1.4		12		940
3/5/2015					10					2.3		15		1300
4/28/2015					10					1.1		0.3		780
10/21/2015					30					2.5		10		1400
PRC-03														
8/12/2015					30					10		10		1300
PTC-01														
10/20/2014					9.4					1.4		12		160
2/24/2015					10					1		2.8		170
4/28/2015					10					1		0.3		110

Table I.1-2 (continued)

		Detected Analytes								
Surface Water Stream Sampling Locations & Date	**Thallium, Dissolved (µg/L)**	**Thallium, Total Recoverable (µg/L)**	**Tin, Dissolved (µg/L)**	**Tin, Total Recoverable (µg/L)**	**Uranium, Dissolved (µg/L)**	**Uranium, Total Recoverable (µg/L)**	**Vanadium, Dissolved (µg/L)**	**Vanadium Total Recoverable (µg/L)**	**Zinc, Dissolved (µg/L)**	**Zinc, Total Recoverable (µg/L)**
PNC-03										
10/21/2014		0.3				0.23		0.45		10
3/4/2015		0.2				1.37		1.6		30
4/29/2015		0.1				0.297		1.6		10
8/11/2015		1				1.6		10		30
10/20/2015		1				0.4		0.68		30
PNC-04										
10/20/2014		0.6				0.46		0.43		20
3/2/2015		0.1				0.74		1.1		15
4/27/2015		0.1				0.238		1.5		10
8/11/2015		1				1.5		10		30
10/20/2015		1				0.48		0.81		30
PRC-01										
10/21/2014		0.6				1.85		0.74		20
2/26/2015		0.2				2.6		0.93		54
4/29/2015		0.1				0.108		2		10
8/12/2015		0.47				0.98		10		30
10/20/2015		1				0.53		1.1		30
PRC-02										
10/20/2014		0.3				0.92		0.63		10
3/5/2015		0.1				1.4		0.89		15
4/28/2015		0.1				0.105		2.3		10
10/21/2015		1				0.5		1.2		30
PRC-03										
8/12/2015		1				1.5		10		30
PTC-01										
10/20/2014		0.3				0.26		0.3		10
2/24/2015		0.1				0.6		0.77		10
4/28/2015		0.1				0.303		1.3		10

Table I.1-3
Non-Stream Surface Water Sampling Water Quality
White Pine Copper LLC

	Detected Analytes															
Surface Water Non-Stream Sampling Locations & Date	**Silver, Total Recoverable (µg/L)**	**Aluminum, Total Recoverable (µg/L)**	**Aluminum, Dissolved (µg/L)**	**Ammonia (mg/L)**	**Bromide (mg/L)**	**Carbon, Dissolved Organic (mg/L)**	**Total Organic Carbon (TOC) (mg/L)**	**Fluoride (mg/L)**	**Nitrate as N (mg/L)**	**Nitrate/Nitrite as N (N) (mg/L)**	**Nitrite as N (mg/L)**	**Sodium, Dissolved (µg/L)**	**Sodium, Total Recoverable (µg/L)**	**Sulfate (mg/L)**	**Sulfide (mg/L)**	**Total Dissolved Solids (mg/L)**
BCE-01																
10/21/2014	12						7.6			2.2				3		110
4/29/2015	0.3						6.6			0.1				3		130
8/13/2015	10															
10/26/2015	10						8.9			0.4				6		110
BCW-01																
10/20/2014	12						7.6			0.11				3		120
2/24/2015	16.7						24			0.2				16.6		310
4/29/2015	0.3						7.2			0.1				3		130
8/13/2015	10															
10/26/2015	20						16.4			0.6				12		280
BDP-01																
10/14/2014	2						4			0.1				45		170
2/25/2015	7.3						3.5			0.35				50		210
4/30/2015	0.3						4			0.1				48		180
8/13/2015	10															
10/26/2015	10						4.6			0.4				51		210
BNC-01																
10/20/2014	12						6			0.1				3		120
2/26/2015	6.7						8.6			0.1				3.4		140
4/28/2015	0.3						6.3			0.1				3		120
8/13/2015	10															
10/26/2015	10						6.9			0.4				6		120
BNE-01																
10/21/2014	12						9.9			0.1				3		340
4/28/2015	0.3						8.5			0.1				3		320
8/11/2015	10															
10/26/2015	10						11			0.4				6		320
BNW-01																
10/20/2014	12						7.4			0.13				6		120
2/26/2015	5.6						8.1			0.1				3.2		140
4/29/2015	0.3						7			0.1				3		140
8/13/2015	10															
10/26/2015	10						7.9			0.2				6		120
CLD_01																
11/19/2014	2															
CLD_02																
11/19/2014	2															
CLD_03																
11/19/2014	2															
CLD_04																
11/19/2014	17.7															
HD-SW01																
10/29/2015	0.77															

Table I.1-3 (continued)

Detected Analytes										Detected						
Surface Water Non-Stream Sampling Locations & Date	Salinity (PSU)	Total Suspended Solids (mg/L)	Total Alkalinity as CaCO3 at pH 4.5 (mg/L)	Antimony, Dissolved (µg/L)	Antimony, Total Recoverable (µg/L)	Arsenic, Total Recoverable (µg/L)	Arsenic, Dissolved (µg/L)	Barium, Dissolved (µg/L)	Barium, Total Recoverable (µg/L)	Beryllium, Dissolved (µg/L)	Beryllium, Total Recoverable (µg/L)	Bicarbonate Alkalinity (as CaCO3) (mg/L)	Boron, Dissolved (µg/L)	Boron, Total Recoverable (µg/L)	Cadmium, Dissolved (µg/L)	Cadmium, Total Recoverable (µg/L)
BCE-01																
10/21/2014					0.25	0.17			38		0.4	85		30		0.1
4/29/2015					0.4	2			40		0.4	110		40		0.1
8/13/2015					10	10			38		2			100		1
10/26/2015					10	10			39		2	99		100		1
BCW-01																
10/20/2014					0.25	0.17			25		0.4	98		63		0.1
2/24/2015					0.4	2			135		0.8	240		80		0.2
4/29/2015					0.4	2			37		0.4	100		40		0.1
8/13/2015					10	10			38		2			100		1
10/26/2015					20	20			61		4	240		200		2
BDP-01																
10/14/2014					1.4	1.2			21		0.4	100		40		1.5
2/25/2015					0.89	1			31		0.4	110		40		0.39
4/30/2015					1.1	2			24		0.4	100		40		0.16
8/13/2015					10	1.4			27		2			100		1
10/26/2015					10	10			30		2	130		41		1
BNC-01																
10/20/2014					0.25	0.17			110		0.4	71		30		0.1
2/26/2015					0.2	1			180		0.4	110		40		0.1
4/28/2015					0.4	2			120		0.4	96		40		0.1
8/13/2015					10	10			100		2			100		1
10/26/2015					10	10			99		2	81		100		1
BNE-01																
10/21/2014					0.25	0.24			140		0.4	110		89		0.1
4/28/2015					0.4	2			71		0.4	95		40		0.1
8/11/2015					10	10			150		2			100		1
10/26/2015					10	10			170		2	130		100		1
BNW-01																
10/20/2014					0.25	0.34			24		0.4	93		47		0.1
2/26/2015					0.2	1			59		0.4	130		40		0.1
4/29/2015					0.4	2			34		0.4	130		40		0.1
8/13/2015					10	10			27		2			100		1
10/26/2015					10	10			30		2	100		100		1
CLD_01																
11/19/2014						0.61			20					38		0.12
CLD_02																
11/19/2014						0.41			21					26		0.071
CLD_03																
11/19/2014						0.49			22					24		0.089
CLD_04																
11/19/2014						0.53			72					78		0.143
HD-SW01																
10/29/2015						1.59			164					80		0.61

Table I.1-3 (continued)

Analytes								Detected Analytes								
Surface Water Non-Stream Sampling Locations & Date	Calcium, Dissolved (µg/L)	Calcium, Total Recoverable (µg/L)	Total Chloride (mg/L)	Chromium, Dissolved (µg/L)	Chromium, Total Recoverable (µg/L)	Cobalt, Dissolved (µg/L)	Cobalt, Total Recoverable (µg/L)	Copper, Dissolved (µg/L)	Total Copper (µg/L)	Cyanide, Total (mg/L)	Hardness (mg/L)	Iron, Dissolved (µg/L)	Total Iron (µg/L)	Lead, Dissolved (µg/L)	Lead, Total Recoverable (µg/L)	Lithium, Dissolved (µg/L)
BCE-01																
10/21/2014			3		0.8		4		0.0056		83		300		10	
4/29/2015			4		6.6		1		0.0086		97		300		0.1	
8/13/2015					5.4		20		0.01		92		390		10	
10/26/2015			6		5.1		10		0.0061		88		300		3	
BCW-01																
10/20/2014			3		0.8		4		8.4		98		62		10	
2/24/2015			15		14.8		6		16		130		3800		0.2	
4/29/2015			4		6.3		1		19		92		340		0.1	
8/13/2015					6.1		20		7.2		110		94		10	
10/26/2015			5		12.6		20		26		110		97		6	
BDP-01																
10/14/2014			7		0.8		1	34	25		130		64		10	
2/25/2015			4		9.9		3		68		160		110		0.1	
4/30/2015			4		14		2		62		130		160		0.1	
8/13/2015					7.7		20		31		130		63		10	
10/26/2015			6		8.6		10		26		150		140		3	
BNC-01																
10/20/2014			11		0.8		4		5.7		82		60		10	
2/26/2015			16		7.5		3		6.3		120		530		12	
4/28/2015			14		6.7		1.2		6.4		91		87		0.1	
8/13/2015					5.6		20		10		81		160		10	
10/26/2015			14		5.5		10		7.2		78		410		3	
BNE-01																
10/21/2014			96		0.8		4		5.1		200		390		10	
4/28/2015			78		14		1.1		8.9		160		320		0.1	
8/11/2015					14		20		5.3		240		950		10	
10/26/2015			140		15		4.7		12		250		390		3	
BNW-01																
10/20/2014			3		0.8		4		4.9		90		49		10	
2/26/2015			3		8.1		3		8.6		130		110		0.1	
4/29/2015			19		7.4		1		9.2		110		86		0.1	
8/13/2015					4.9		20		3.6		81		120		10	
10/26/2015			4		5.7		10		6.2		92		96		3	
CLD_01																
11/19/2014			6		0.8				34.1				950		0.43	
CLD_02																
11/19/2014			12		0.8				36.3				960		0.35	
CLD_03																
11/19/2014			6		0.8				37.1				1000		0.4	
CLD_04																
11/19/2014			180		1.6				35.4				410		0.35	
HD-SW01																
10/29/2015			43		11.2				17				20000		10.1	

Table I.1-3 (continued)

								Detected Analytes								
Surface Water Non-Stream Sampling Locations & Date	**Lithium, Total Recoverable (µg/L)**	**Manganese, Dissolved (µg/L)**	**Manganese, Total Recoverable (µg/L)**	**Magnesium, Dissolved (µg/L)**	**Magnesium, Total Recoverable (µg/L)**	**Methyl Mercury, Dissolved (ng/L)**	**Methyl Mercury, Total Recoverable (ng/L)**	**Molybdenum, Dissolved (µg/L)**	**Molybdenum, Total Recoverable (µg/L)**	**Nickel, Dissolved (µg/L)**	**Nickel, Total Recoverable (µg/L)**	**pH**	**Phosphorus-Total (as P) (mg/L)**	**Potassium, Dissolved (µg/L)**	**Potassium, Total Recoverable (µg/L)**	**Selenium, Dissolved (µg/L)**
BCE-01																
10/21/2014	6		57								8					
4/29/2015	6		25								10					
8/13/2015	30		63								30					
10/26/2015	6.7		47								30					
BCW-01																
10/20/2014	6		10								8					
2/24/2015	12		2700								20					
4/29/2015	6		31								10					
8/13/2015	7.1		40								30					
10/26/2015	22		20.7								60					
BDP-01																
10/14/2014	6		0.5								5.6					
2/25/2015	12		51								10					
4/30/2015	8.1		30								10					
8/13/2015	11		29								30					
10/26/2015	16		11								30					
BNC-01																
10/20/2014	6		0.5								8					
2/26/2015	6.1		1000								10					
4/28/2015	6		22								10					
8/13/2015	8		46								30					
10/26/2015	11		51								30					
BNE-01																
10/21/2014	6		48								19					
4/28/2015	8.6		55								10					
8/11/2015	13		230								30					
10/26/2015	19		46								30					
BNW-01																
10/20/2014	6		7.1								9.3					
2/26/2015	6		92								10					
4/29/2015	6		45								10					
8/13/2015	30		46								30					
10/26/2015	8.3		14								30					
CLD_01																
11/19/2014	6		20													
CLD_02																
11/19/2014	6		21													
CLD_03																
11/19/2014	6		23													
CLD_04																
11/19/2014	12		176													
HD-SW01																
10/29/2015	12.3		550													

Table I.1-3 (continued)

						Detected Analytes								
Surface Water Non-Stream Sampling Locations & Date	**Selenium, Total Recoverable (µg/L)**	**Silver, Dissolved (µg/L)**	**Strontium, Dissolved (µg/L)**	**Strontium, Total Recoverable (µg/L)**	**Thallium, Dissolved (µg/L)**	**Thallium, Total Recoverable (µg/L)**	**Tin, Dissolved (µg/L)**	**Tin, Total Recoverable (µg/L)**	**Uranium, Dissolved (µg/L)**	**Uranium, Total Recoverable (µg/L)**	**Vanadium, Dissolved (µg/L)**	**Total Vanadium (µg/L)**	**Zinc, Dissolved (µg/L)**	**Zinc, Total Recoverable (µg/L)**
BCE-01														
10/21/2014	1.4			63		0.3				0.23		0.3		10
4/29/2015	1			64		0.1				0.13		0.77		10
8/13/2015	10			65		1				0.051		10		30
10/26/2015	10			65		1				0.066		3		30
BCW-01														
10/20/2014	1.4			110		0.3				0.23		0.3		10
2/24/2015	2			300		0.2				0.46		0.6		25
4/29/2015	1			110		0.1				0.133		0.7		10
8/13/2015	10			140		1				0.017		10		30
10/26/2015	20			280		1.21				0.128		3		60
BDP-01														
10/14/2014	1.4			79		0.3				0.38		0.3		10
2/25/2015	1			86		0.1				0.47		0.66		44
4/30/2015	1			76		0.1				0.466		0.97		10
8/13/2015	10			74		1				0.57		10		30
10/26/2015	10			94		1				0.66		1.5		30
BNC-01														
10/20/2014	1.4			130		0.3				0.23		0.3		10
2/26/2015	1			170		0.1				0.23		0.42		10
4/28/2015	1			130		0.1				0.131		0.83		10
8/13/2015	10			130		0.54				0.017		10		30
10/26/2015	10			150		1				0.049		0.72		30
BNE-01														
10/21/2014	1.5			420		0.3				0.23		0.3		10
4/28/2015	1			290		0.1				0.13		1.2		10
8/11/2015	10			500		1				0.011		10		30
10/26/2015	1.1			580		1				0.083		0.73		30
BNW-01														
10/20/2014	1.4			81		0.3				0.23		0.3		10
2/26/2015	1			110		0.1				0.23		0.4		10
4/29/2015	1			89		0.1				0.238		1		10
8/13/2015	10			80		1				0.31		10		30
10/26/2015	10			92		1				0.41		0.66		30
CLD_01														
11/19/2014	0.44			34									10	
CLD_02														
11/19/2014	0.044			37									10	
CLD_03														
11/19/2014	0.51			35									10	
CLD_04														
11/19/2014	0.88			220									20	
HD-SW01														
10/29/2015	1			153										98

Table I.1-3 (continued)

Detected Analytes																
Surface Water Non-Stream Sampling Locations & Date	**Silver, Total Recoverable (µg/L)**	**Aluminum, Total Recoverable (µg/L)**	**Aluminum, Dissolved (µg/L)**	**Ammonia (mg/L)**	**Bromide (mg/L)**	**Carbon, Dissolved Organic (mg/L)**	**Total Organic Carbon (TOC) (mg/L)**	**Fluoride (mg/L)**	**Nitrate as N (mg/L)**	**Nitrate/Nitrite as N (N) (mg/L)**	**Nitrite as N (mg/L)**	**Sodium, Dissolved (µg/L)**	**Sodium, Total Recoverable (µg/L)**	**Sulfate (mg/L)**	**Sulfide (mg/L)**	**Total Dissolved Solids (mg/L)**
MDEQ-1 (SW)																
7/29/1997	0.25															
MDEQ-2 (SW)																
7/29/1997	0.25															
MDEQ-3 (SW)																
7/29/1997	0.25															
N2D-01																
10/14/2014	7.1						5.1			0.1				27		1000
NBT-01																
4/29/2015	0.3						1.4			0.27				150		600
Perch Creek Pond																
5/15/2024	0.5						3.8									780
Pine Creek																
4/4/2021																
5/24/2021									0.1		0.1			33		
Portage Creek																
5/2/2022																100
SBD-01																
10/14/2014	2						8.4			0.1				3		150
2/25/2015	7.8						16			0.1				10		220
4/29/2015	0.3						7.7			0.1				3		100
8/13/2015	4.2															
10/26/2015	10						9.7			0.4				6		170
SBE-01																
10/22/2014	12						6.1			0.1				3		100
4/30/2015	0.3						7.1			0.1				3		110
8/13/2015	10															
10/26/2015	10						7.4			0.4				6		110
SBW-01																
10/21/2014	12						5.4			0.18				3		120
2/25/2015	5.5						7.5			0.35				3.8		140
4/29/2015	0.3						6			0.1				3		140
8/13/2015	2.7															
10/26/2015	10						6.9			0.4				6		110
SBW26																
8/2/1997	0.8															

Table I.1-3 (continued)

Detected Analytes										Detected						
Surface Water Non-Stream Sampling Locations & Date	**Salinity (PSU)**	**Total Suspended Solids (mg/L)**	**Total Alkalinity as CaCO3 at pH 4.5 (mg/L)**	**Antimony, Dissolved (µg/L)**	**Antimony, Total Recoverable (µg/L)**	**Arsenic, Total Recoverable (µg/L)**	**Arsenic, Dissolved (µg/L)**	**Barium, Dissolved (µg/L)**	**Barium, Total Recoverable (µg/L)**	**Beryllium, Dissolved (µg/L)**	**Beryllium, Total Recoverable (µg/L)**	**Bicarbonate Alkalinity (as CaCO3) (mg/L)**	**Boron, Dissolved (µg/L)**	**Boron, Total Recoverable (µg/L)**	**Cadmium, Dissolved (µg/L)**	**Cadmium, Total Recoverable (µg/L)**
MDEQ-1 (SW)																
7/29/1997						2.5			100					130		0.6
MDEQ-2 (SW)																
7/29/1997						2.5			100					25		0.25
MDEQ-3 (SW)																
7/29/1997						11			100					70		0.25
N2D-01																
10/14/2014					0.2	0.17			610		0.4	170		210		0.1
NBT-01																
4/29/2015					0.4	2			72		0.4	240		560		0.1
Perch Creek Pond																
5/15/2024		12				1										0.2
Pine Creek																
4/4/2021																
5/24/2021		10														
Portage Creek																
5/2/2022		8														
SBD-01																
10/14/2014					0.25	0.17			39		0.4	120		64		0.1
2/25/2015					0.2	1			79		0.4	140		40		0.1
4/29/2015					0.4	2			30		0.4	73		40		0.1
8/13/2015					10	10			39		2			100		1
10/26/2015					10	10			45		2	130		100		1
SBE-01																
10/22/2014					0.25	0.17			12		0.4	84		30		0.1
4/30/2015					0.4	2			8.7		0.4	100		40		0.1
8/13/2015					10	10			31		2			100		1
10/26/2015					10	10			23		2	97		100		1
SBW-01																
10/21/2014					0.25	0.17			45		0.4	100		30		0.1
2/25/2015					0.2	1			63		0.4	130		40		0.1
4/29/2015					0.4	2			39		0.4	120		40		0.1
8/13/2015					10	1.2			24		2			100		1
10/26/2015					10	10			34		2	100		100		1
SBW26																
8/2/1997						6			100					60		0.25

Table I.1-3 (continued)

Analytes								Detected Analytes								
Surface Water Non-Stream Sampling Locations & Date	**Calcium, Dissolved (µg/L)**	**Calcium, Total Recoverable (µg/L)**	**Total Chloride (mg/L)**	**Chromium, Dissolved (µg/L)**	**Chromium, Total Recoverable (µg/L)**	**Cobalt, Dissolved (µg/L)**	**Cobalt, Total Recoverable (µg/L)**	**Copper, Dissolved (µg/L)**	**Total Copper (µg/L)**	**Cyanide, Total (mg/L)**	**Hardness (mg/L)**	**Iron, Dissolved (µg/L)**	**Total Iron (µg/L)**	**Lead, Dissolved (µg/L)**	**Lead, Total Recoverable (µg/L)**	**Lithium, Dissolved (µg/L)**
MDEQ-1 (SW)																
7/29/1997					25				330						1.5	
MDEQ-2 (SW)																
7/29/1997					25				85						1.5	
MDEQ-3 (SW)																
7/29/1997					25				500						1.5	
N2D-01																
10/14/2014			360		0.8		1	3.7	2		590		440		10	
NBT-01																
4/29/2015			39		24		1.5		21		370		420		0.1	
Perch Creek Pond																
5/15/2024			270					13	18		300					
Pine Creek																
4/4/2021																
5/24/2021			190							0.005						
Portage Creek																
5/2/2022			10					84			50					
SBD-01																
10/14/2014					0.8		1	2							10	
2/25/2015					9.7		3								0.1	
4/29/2015					6		1								0.12	
8/13/2015					5.3		20								10	
10/26/2015					7.9		10								3	
SBE-01																
10/22/2014			3		0.8		4		5.1		84		46		10	
4/30/2015			4		6.2		2		7.9		92		140		0.1	
8/13/2015					5.9		20		3.8		88		150		10	
10/26/2015			7		5		10		5.9		91		46		3	
SBW-01																
10/21/2014			3		0.8		4		20		96		130		10	
2/25/2015			3		8.8		3		25		130		920		0.1	
4/29/2015			4		7.9		1		15		100		200		0.1	
8/13/2015					4		20		9.9		64		82		10	
10/26/2015			10		5.8		10		14		87		64		3	
SBW26																
8/2/1997					25				880						20	

Table I.1-3 (continued)

								Detected Analytes								
Surface Water Non-Stream Sampling Locations & Date	**Lithium, Total Recoverable (µg/L)**	**Manganese, Dissolved (µg/L)**	**Manganese, Total Recoverable (µg/L)**	**Magnesium, Dissolved (µg/L)**	**Magnesium, Total Recoverable (µg/L)**	**Methyl Mercury, Dissolved (ng/L)**	**Methyl Mercury, Total Recoverable (ng/L)**	**Molybdenum, Dissolved (µg/L)**	**Molybdenum, Total Recoverable (µg/L)**	**Nickel, Dissolved (µg/L)**	**Nickel, Total Recoverable (µg/L)**	**pH**	**Phosphorus-Total (as P) (mg/L)**	**Potassium, Dissolved (µg/L)**	**Potassium, Total Recoverable (µg/L)**	**Selenium, Dissolved (µg/L)**
MDEQ-1 (SW)																
7/29/1997	41		60								25					
MDEQ-2 (SW)																
7/29/1997	2.5		70								25					
MDEQ-3 (SW)																
7/29/1997	59		50								25					
N2D-01																
10/14/2014	6		1100								30					
NBT-01																
4/29/2015	110		310								10					
Perch Creek Pond																
5/15/2024												7.7				
Pine Creek																
4/4/2021																
5/24/2021												7.8				
Portage Creek																
5/2/2022												7.02				
SBD-01																
10/14/2014	6		0.5								5.7					
2/25/2015	11		1100								10					
4/29/2015	6		26								10					
8/13/2015	12		32								30					
10/26/2015	17		11								30					
SBE-01																
10/22/2014	6		0.5								11					
4/30/2015	6		28								10					
8/13/2015	30		36								30					
10/26/2015	7.8		3.4								30					
SBW-01																
10/21/2014	6		0.5								8					
2/25/2015	6		320								10					
4/29/2015	6		33								10					
8/13/2015	30		20								30					
10/26/2015	9.7		5.9								30					
SBW26																
8/2/1997	2.5		4900								25					

Table I.1-3 (continued)

						Detected Analytes								
Surface Water Non-Stream Sampling Locations & Date	**Selenium, Total Recoverable (µg/L)**	**Silver, Dissolved (µg/L)**	**Strontium, Dissolved (µg/L)**	**Strontium, Total Recoverable (µg/L)**	**Thallium, Dissolved (µg/L)**	**Thallium, Total Recoverable (µg/L)**	**Tin, Dissolved (µg/L)**	**Tin, Total Recoverable (µg/L)**	**Uranium, Dissolved (µg/L)**	**Uranium, Total Recoverable (µg/L)**	**Vanadium, Dissolved (µg/L)**	**Total Vanadium (µg/L)**	**Zinc, Dissolved (µg/L)**	**Zinc, Total Recoverable (µg/L)**
MDEQ-1 (SW)														
7/29/1997	2.5			110										360
MDEQ-2 (SW)														
7/29/1997	2.5			130										10
MDEQ-3 (SW)														
7/29/1997	2.5			160										420
N2D-01														
10/14/2014	37			1400		0.3				0.39		0.3		10
NBT-01														
4/29/2015	1			980		0.1				0.518		1		260
Perch Creek Pond														
5/15/2024	1													
Pine Creek														
4/4/2021														
5/24/2021														
Portage Creek														
5/2/2022														
SBD-01														
10/14/2014	25			240		0.3				0.5		0.3		10
2/25/2015	1			270		0.1				0.46		2		13
4/29/2015	1			120		0.1				0.342		1.4		10
8/13/2015	10			200		1				0.21		10		30
10/26/2015	10			250		0.19				0.85		0.98		30
SBE-01														
10/22/2014	1.4			62		0.3				0.23		0.3		10
4/30/2015	1			43		0.1				0.127		0.65		10
8/13/2015	10			73		1				0.045		10		30
10/26/2015	10			70		1				0.089		0.67		30
SBW-01														
10/21/2014	1.4			84		0.3				0.23		0.3		10
2/25/2015	1			92		0.1				0.23		0.8		11
4/29/2015	1			79		0.1				0.157		0.86		10
8/13/2015	10			61		1				0.1		10		30
10/26/2015	10			84		1				0.16		0.62		30
SBW26														
8/2/1997	2.5			110										190

Table I.1-3 (continued)

Surface Water Non-Stream Sampling Locations & Date	Detected Analytes																
	Silver, Total Recoverable (µg/L)	Aluminum, Total Recoverable (µg/L)	Aluminum, Dissolved (µg/L)	Ammonia (mg/L)	Bromide (mg/L)	Carbon, Dissolved Organic (mg/L)	Total Organic Carbon (TOC) (mg/L)	Fluoride (mg/L)	Nitrate as N (mg/L)	Nitrate/Nitrite as N (N) (mg/L)	Nitrite as N (mg/L)	Sodium, Dissolved (µg/L)	Sodium, Total Recoverable (µg/L)	Sulfate (mg/L)	Sulfide (mg/L)	Total Dissolved Solids (mg/L)
SBW28																	
8/2/1997	8																
SW1																	
4/10/1998																	
SW10																	
7/29/1997	0.25																
4/9/1998																	
SW11																	
8/2/1997	0.25																
SW12																	
7/29/1997	0.25																
SW13																	
7/30/1997	0.25																
SW14																	
8/1/1997	0.25																
4/15/1998																	
SW15																	
8/2/1997	0.25																
4/10/1998																	
SW16																	
8/5/1997	0.25																
8/20/1997	0.25																
SW17																	
8/5/1997	0.25																
SW18																	
8/5/1997	0.25																
8/21/1997	0.25																
SW19																	
8/5/1997																	
SW2																	
8/2/1997																	
8/20/1997																	
4/10/1998																	
SW20																	
8/4/1997	0.25																
8/22/1997	0.25																
4/9/1998																	
8/11/1998																	
SW21																	
8/4/1997	0.25																
SW22																	
8/4/1997	0.25																
SW23																	
8/4/1997	0.25																
8/22/1997	0.25																
4/9/1998																	
8/11/1998																	
SW24																	
7/30/1997																	
SW25																	
8/2/1997	0.25																
SW26																	
8/1/1997	0.25																
SW27																	
8/6/1997	0.25																
SW28																	
8/20/1997																	
4/10/1998																	
SW29																	

Table I.1-3 (continued)

Detected Analytes										Detected						
Surface Water Non-Stream Sampling Locations & Date	Salinity (PSU)	Total Suspended Solids (mg/L)	Total Alkalinity as CaCO3 at pH 4.5 (mg/L)	Antimony, Dissolved (µg/L)	Antimony, Total Recoverable (µg/L)	Arsenic, Total Recoverable (µg/L)	Arsenic, Dissolved (µg/L)	Barium, Dissolved (µg/L)	Barium, Total Recoverable (µg/L)	Beryllium, Dissolved (µg/L)	Beryllium, Total Recoverable (µg/L)	Bicarbonate Alkalinity (as CaCO3) (mg/L)	Boron, Dissolved (µg/L)	Boron, Total Recoverable (µg/L)	Cadmium, Dissolved (µg/L)	Cadmium, Total Recoverable (µg/L)
SBW28																
8/2/1997						460			2800					340		44
SW1																
4/10/1998																
SW10																
7/29/1997						2.5			100					25		0.9
4/9/1998																1.6
SW11																
8/2/1997						2.5			100					80		0.25
SW12																
7/29/1997						2.5			100					25		0.25
SW13																
7/30/1997						2.5			100					570		1.6
SW14																
8/1/1997						2.5			100					70		0.25
4/15/1998																
SW15																
8/2/1997						2.5			100					25		0.25
4/10/1998									100							
SW16																
8/5/1997						2.5			100					110		0.25
8/20/1997						10			100							0.25
SW17																
8/5/1997						2.5			100					70		1.2
SW18																
8/5/1997						2.5			100					25		0.25
8/21/1997						10			100							1
SW19																
8/5/1997																
SW2																
8/2/1997																
8/20/1997																
4/10/1998																
SW20																
8/4/1997						2.5			100					25		0.5
8/22/1997						2.5			100							0.25
4/9/1998																
8/11/1998									26					30		0.9
SW21																
8/4/1997						0.5			100					25		0.25
SW22																
8/4/1997						2.5			100					25		1.1
SW23																
8/4/1997						2.5			100					25		0.25
8/22/1997						20			100							1
4/9/1998																
8/11/1998									159					70		0.6
SW24																
7/30/1997																
SW25																
8/2/1997						2.5			100					25		0.25
SW26																
8/1/1997						2.5			100					25		0.25
SW27																
8/6/1997						2.5			100					60		7.8
SW28																
8/20/1997																
4/10/1998									100							
SW29																

Table I.1-3 (continued)

Analytes								Detected Analytes								
Surface Water Non-Stream Sampling Locations & Date	Calcium, Dissolved (µg/L)	Calcium, Total Recoverable (µg/L)	Total Chloride (mg/L)	Chromium, Dissolved (µg/L)	Chromium, Total Recoverable (µg/L)	Cobalt, Dissolved (µg/L)	Cobalt, Total Recoverable (µg/L)	Copper, Dissolved (µg/L)	Total Copper (µg/L)	Cyanide, Total (mg/L)	Hardness (mg/L)	Iron, Dissolved (µg/L)	Total Iron (µg/L)	Lead, Dissolved (µg/L)	Lead, Total Recoverable (µg/L)	Lithium, Dissolved (µg/L)
SBW28																
8/2/1997					710				11000						240	
SW1																
4/10/1998											29					
SW10																
7/29/1997					25				170						27	
4/9/1998									330						1	
SW11																
8/2/1997					25				32						1.5	
SW12																
7/29/1997					25				110						1.5	
SW13																
7/30/1997					25				140						1.5	
SW14																
8/1/1997					25				73						1.5	
4/15/1998																
SW15																
8/2/1997					0.025				56		90				1.5	
4/10/1998									90		34					
SW16																
8/5/1997					25				12.5		283				1.5	
8/20/1997					25				12.5		303				2	
SW17																
8/5/1997					25				12.5		121				1.5	
SW18																
8/5/1997					25				12.5		108				1.5	
8/21/1997					25				12.5		107				1.5	
SW19																
8/5/1997											174					
SW2																
8/2/1997											87					
8/20/1997																
4/10/1998											27					
SW20																
8/4/1997					25				12.5		123				1.5	
8/22/1997					25				12.5		80				3	
4/9/1998											23					
8/11/1998											89				2	
SW21																
8/4/1997					25				12.5		215				1.5	
SW22																
8/4/1997					25				12.5		223				1.5	
SW23																
8/4/1997					25				12.5		224				1.5	
8/22/1997					25				12.5		267				1.5	
4/9/1998											66					
8/11/1998											357				5	
SW24																
7/30/1997																
SW25																
8/2/1997					25				60						1.5	
SW26																
8/1/1997					25				110						1.5	
SW27																
8/6/1997					25				11,000						1.5	
SW28																
8/20/1997											104					
4/10/1998									90		41					
SW29																

Table I.1-3 (continued)

								Detected Analytes								
Surface Water Non-Stream Sampling Locations & Date	**Lithium, Total Recoverable (µg/L)**	**Manganese, Dissolved (µg/L)**	**Manganese, Total Recoverable (µg/L)**	**Magnesium, Dissolved (µg/L)**	**Magnesium, Total Recoverable (µg/L)**	**Methyl Mercury, Dissolved (ng/L)**	**Methyl Mercury, Total Recoverable (ng/L)**	**Molybdenum, Dissolved (µg/L)**	**Molybdenum, Total Recoverable (µg/L)**	**Nickel, Dissolved (µg/L)**	**Nickel, Total Recoverable (µg/L)**	**pH**	**Phosphorus-Total (as P) (mg/L)**	**Potassium, Dissolved (µg/L)**	**Potassium, Total Recoverable (µg/L)**	**Selenium, Dissolved (µg/L)**
SBW28																
8/2/1997	1500		8000								650					
SW1																
4/10/1998																
SW10																
7/29/1997	7		30								25					
4/9/1998	6		70								25					
SW11																
8/2/1997	2.5		90								25					
SW12																
7/29/1997	2.5		50								25					
SW13																
7/30/1997	60		10								25					
SW14																
8/1/1997	2.5		90								25					
4/15/1998																
SW15																
8/2/1997	2.5		90								25					
4/10/1998	2.5		30													
SW16																
8/5/1997	36		80								25					
8/20/1997											25					
SW17																
8/5/1997	8		20								25					
SW18																
8/5/1997	5		500								25					
8/21/1997											25					
SW19																
8/5/1997																
SW2																
8/2/1997																
8/20/1997																
4/10/1998																
SW20																
8/4/1997	2.5		2000								25					
8/22/1997											25					
4/9/1998																
8/11/1998	20		493													
SW21																
8/4/1997	13		70								25					
SW22																
8/4/1997	15		360								25					
SW23																
8/4/1997	14		430								25					
8/22/1997											25					
4/9/1998																
8/11/1998	20		841													
SW24																
7/30/1997																
SW25																
8/2/1997	20		10								25					
SW26																
8/1/1997	2.5		120								25					
SW27																
8/6/1997	28		790								25					
SW28																
8/20/1997																
4/10/1998	2.5		40													
SW29																

Table I.1-3 (continued)

						Detected Analytes								
Surface Water Non-Stream Sampling Locations & Date	**Selenium, Total Recoverable (µg/L)**	**Silver, Dissolved (µg/L)**	**Strontium, Dissolved (µg/L)**	**Strontium, Total Recoverable (µg/L)**	**Thallium, Dissolved (µg/L)**	**Thallium, Total Recoverable (µg/L)**	**Tin, Dissolved (µg/L)**	**Tin, Total Recoverable (µg/L)**	**Uranium, Dissolved (µg/L)**	**Uranium, Total Recoverable (µg/L)**	**Vanadium, Dissolved (µg/L)**	**Total Vanadium (µg/L)**	**Zinc, Dissolved (µg/L)**	**Zinc, Total Recoverable (µg/L)**
SBW28														
8/2/1997	110			510										2500
SW1														
4/10/1998														
SW10														
7/29/1997	2.5			50										10
4/9/1998				70										70
SW11														
8/2/1997	2.5			100										40
SW12														
7/29/1997	2.5			120										50
SW13														
7/30/1997	2.5			250										90
SW14														
8/1/1997	2.5			180										60
4/15/1998														
SW15														
8/2/1997	2.5			80										10
4/10/1998				30										
SW16														
8/5/1997	2.5			1670										10
8/20/1997														30
SW17														
8/5/1997	2.5			520										10
SW18														
8/5/1997	2.5			230										10
8/21/1997														20
SW19														
8/5/1997														
SW2														
8/2/1997														
8/20/1997														
4/10/1998														
SW20														
8/4/1997	2.5			100										10
8/22/1997														10
4/9/1998														
8/11/1998	1			70										
SW21														
8/4/1997	2.5			610										10
SW22														
8/4/1997	2.5			840										10
SW23														
8/4/1997	0.25			790										10
8/22/1997														10
4/9/1998														
8/11/1998	1			1010										
SW24														
7/30/1997														
SW25														
8/2/1997	2.5			40										10
SW26														
8/1/1997	2.5			150										190
SW27														
8/6/1997	2.5			260										620
SW28														
8/20/1997														
4/10/1998				30										
SW29														

Table I.1-3 (continued)

Surface Water Non-Stream Sampling Locations & Date	Detected Analytes																
	Silver, Total Recoverable (µg/L)	Aluminum, Total Recoverable (µg/L)	Aluminum, Dissolved (µg/L)	Ammonia (mg/L)	Bromide (mg/L)	Carbon, Dissolved Organic (mg/L)	Total Organic Carbon (TOC) (mg/L)	Fluoride (mg/L)	Nitrate as N (mg/L)	Nitrate/Nitrite as N (N) (mg/L)	Nitrite as N (mg/L)	Sodium, Dissolved (µg/L)	Sodium, Total Recoverable (µg/L)	Sulfate (mg/L)	Sulfide (mg/L)	Total Dissolved Solids (mg/L)
8/20/1997	0.25																
SW3																	
8/2/1997	0.25																
4/10/1998																	
SW30																	
8/20/1997																	
SW31																	
8/20/1997	0.25																
9/8/1997	0.25																
SW32																	
8/21/1997																	
4/10/1998																	
SW33																	
8/21/1997																	
SW34																	
8/22/1997																	
4/9/1998																	
SW35																	
9/9/1997	1.25																
SW4																	
8/2/1997	0.25																
4/10/1998																	
SW42																	
4/9/1998																	
SW43																	
8/11/1998																	
SW44																	
4/9/1998																	
SW45																	
4/15/1998																	
SW5																	
8/5/1997																	
4/10/1998																	
8/11/1998																	
SW51																	
8/11/1998																	
SW52																	
8/11/1998																	
SW53																	
8/11/1998																	
SW6																	
8/6/1997																	
8/21/1997																	
4/10/1998																	
SW7																	
8/6/1997	0.25																
SW8																	
7/30/1997	0.25																
SW9																	
7/29/1997	0.25																
TBN-01																	
TBS-01																	
UGD-01																	
9/22/2014	50						2.3			0.1				220		2500	
4/29/2015	0.3						2.5			0.1				210		2900	
8/13/2015	10																
10/27/2015	10						3.2			0.2				210		2400	

Table I.1-3 (continued)

Detected Analytes																Detected
Surface Water Non-Stream Sampling Locations & Date	**Salinity (PSU)**	**Total Suspended Solids (mg/L)**	**Total Alkalinity as CaCO3 at pH 4.5 (mg/L)**	**Antimony, Dissolved (µg/L)**	**Antimony, Total Recoverable (µg/L)**	**Arsenic, Total Recoverable (µg/L)**	**Arsenic, Dissolved (µg/L)**	**Barium, Dissolved (µg/L)**	**Barium, Total Recoverable (µg/L)**	**Beryllium, Dissolved (µg/L)**	**Beryllium, Total Recoverable (µg/L)**	**Bicarbonate Alkalinity (as CaCO3) (mg/L)**	**Boron, Dissolved (µg/L)**	**Boron, Total Recoverable (µg/L)**	**Cadmium, Dissolved (µg/L)**	**Cadmium, Total Recoverable (µg/L)**
8/20/1997						10			100							0.25
SW3																
8/2/1997						2.5			100					25		1.2
4/10/1998									100							
SW30																
8/20/1997																
SW31																
8/20/1997						10			100							2
9/8/1997						2.5			100					25		0.25
SW32																
8/21/1997																
4/10/1998																
SW33																
8/21/1997																
SW34																
8/22/1997																
4/9/1998																
SW35																
9/9/1997						27.5			500					150		96
SW4																
8/2/1997						2.5			100					25		0.25
4/10/1998									100							
SW42																
4/9/1998																
SW43																
8/11/1998																
SW44																
4/9/1998																
SW45																
4/15/1998																
SW5																
8/5/1997																
4/10/1998																
8/11/1998																
SW51																
8/11/1998									59					50		0.6
SW52																
8/11/1998									38					30		0.6
SW53																
8/11/1998									37					30		0.6
SW6																
8/6/1997																
8/21/1997																
4/10/1998																
SW7																
8/6/1997						2.5			100					25		0.25
SW8																
7/30/1997						2.5			100					25		0.25
SW9																
7/29/1997						2.5			100					25		0.25
TBN-01																
TBS-01																
UGD-01																
9/22/2014					20	150			55		1.5	110		1900		97
4/29/2015					0.56	2			60		0.4	110		2100		0.67
8/13/2015					10	1.1			62		2			1900		0.67
10/27/2015					10	1.1			66		2	100		2300		0.52

Table I.1-3 (continued)

Analytes								Detected Analytes								
Surface Water Non-Stream Sampling Locations & Date	**Calcium, Dissolved (µg/L)**	**Calcium, Total Recoverable (µg/L)**	**Total Chloride (mg/L)**	**Chromium, Dissolved (µg/L)**	**Chromium, Total Recoverable (µg/L)**	**Cobalt, Dissolved (µg/L)**	**Cobalt, Total Recoverable (µg/L)**	**Copper, Dissolved (µg/L)**	**Total Copper (µg/L)**	**Cyanide, Total (mg/L)**	**Hardness (mg/L)**	**Iron, Dissolved (µg/L)**	**Total Iron (µg/L)**	**Lead, Dissolved (µg/L)**	**Lead, Total Recoverable (µg/L)**	**Lithium, Dissolved (µg/L)**
8/20/1997					25				42						5	
SW3																
8/2/1997					25				46		87				1.5	
4/10/1998									43		28					
SW30																
8/20/1997											110					
SW31																
8/20/1997					25				420						1.5	
9/8/1997					25				180						8	
SW32																
8/21/1997											245					
4/10/1998											60					
SW33																
8/21/1997											112					
SW34																
8/22/1997											51					
4/9/1998											31					
SW35																
9/9/1997					125				5,000						18	
SW4																
8/2/1997					25				64		89				1.5	
4/10/1998									80		32					
SW42																
4/9/1998											62					
SW43																
8/11/1998											204					
SW44																
4/9/1998											43					
SW45																
4/15/1998																
SW5																
8/5/1997											105					
4/10/1998											40					
8/11/1998											121					
SW51																
8/11/1998											123				1	
SW52																
8/11/1998											99				1	
SW53																
8/11/1998											90				1	
SW6																
8/6/1997											279					
8/21/1997											241					
4/10/1998											54					
SW7																
8/6/1997					25										1.5	
SW8																
7/30/1997					25										1.5	
SW9																
7/29/1997					25										1.5	
TBN-01																
TBS-01																
UGD-01																
9/22/2014			1100		0.6		1	77	140		760		430		30	
4/29/2015			1100		70		2.2		170				220		0.1	
8/13/2015					74		20		120		750		330		10	
10/27/2015			1100		72		10		140		840		550		3	

Table I.1-3 (continued)

								Detected Analytes								
Surface Water Non-Stream Sampling Locations & Date	**Lithium, Total Recoverable (µg/L)**	**Manganese, Dissolved (µg/L)**	**Manganese, Total Recoverable (µg/L)**	**Magnesium, Dissolved (µg/L)**	**Magnesium, Total Recoverable (µg/L)**	**Methyl Mercury, Dissolved (ng/L)**	**Methyl Mercury, Total Recoverable (ng/L)**	**Molybdenum, Dissolved (µg/L)**	**Molybdenum, Total Recoverable (µg/L)**	**Nickel, Dissolved (µg/L)**	**Nickel, Total Recoverable (µg/L)**	**pH**	**Phosphorus-Total (as P) (mg/L)**	**Potassium, Dissolved (µg/L)**	**Potassium, Total Recoverable (µg/L)**	**Selenium, Dissolved (µg/L)**
8/20/1997											25					
SW3																
8/2/1997	2.5		40								25					
4/10/1998	2.5		20													
SW30																
8/20/1997																
SW31																
8/20/1997											25					
9/8/1997	6		30								25					
SW32																
8/21/1997																
4/10/1998																
SW33																
8/21/1997																
SW34																
8/22/1997																
4/9/1998																
SW35																
9/9/1997	91		2370								320					
SW4																
8/2/1997	2.5		30								25					
4/10/1998	2.5		30													
SW42																
4/9/1998																
SW43																
8/11/1998																
SW44																
4/9/1998																
SW45																
4/15/1998																
SW5																
8/5/1997																
4/10/1998																
8/11/1998																
SW51																
8/11/1998	20		45													
SW52																
8/11/1998	20		18													
SW53																
8/11/1998	20		17													
SW6																
8/6/1997																
8/21/1997																
4/10/1998																
SW7																
8/6/1997	2.5		90								25					
SW8																
7/30/1997	2.5		70								25					
SW9																
7/29/1997	2.5		10								25					
TBN-01																
TBS-01																
UGD-01																
9/22/2014	54		460								59					
4/29/2015	160		130						0.063		10					
8/13/2015	170		120								30					
10/27/2015	180		350								30					

Table I.1-3 (continued)

						Detected Analytes								
Surface Water Non-Stream Sampling Locations & Date	**Selenium, Total Recoverable (µg/L)**	**Silver, Dissolved (µg/L)**	**Strontium, Dissolved (µg/L)**	**Strontium, Total Recoverable (µg/L)**	**Thallium, Dissolved (µg/L)**	**Thallium, Total Recoverable (µg/L)**	**Tin, Dissolved (µg/L)**	**Tin, Total Recoverable (µg/L)**	**Uranium, Dissolved (µg/L)**	**Uranium, Total Recoverable (µg/L)**	**Vanadium, Dissolved (µg/L)**	**Total Vanadium (µg/L)**	**Zinc, Dissolved (µg/L)**	**Zinc, Total Recoverable (µg/L)**
8/20/1997														600
SW3														
8/2/1997	2.5			90										40
4/10/1998				30										
SW30														
8/20/1997														
SW31														
8/20/1997														50
9/8/1997	2.5			60										160
SW32														
8/21/1997														
4/10/1998														
SW33														
8/21/1997														
SW34														
8/22/1997														
4/9/1998														
SW35														
9/9/1997	19.5			650										5500
SW4														
8/2/1997	2.5			100										60
4/10/1998				30										
SW42														
4/9/1998														
SW43														
8/11/1998														
SW44														
4/9/1998														
SW45														
4/15/1998														
SW5														
8/5/1997														
4/10/1998														
8/11/1998														
SW51														
8/11/1998	1			110										
SW52														
8/11/1998	1			80										
SW53														
8/11/1998	1			80										
SW6														
8/6/1997														
8/21/1997														
4/10/1998														
SW7														
8/6/1997	2.5			90										15
SW8														
7/30/1997	2.5			100										60
SW9														
7/29/1997	2.5			40										60
TBN-01														
TBS-01														
UGD-01														
9/22/2014	1.4			3800		20				0.23		7.6		10
4/29/2015	5.6			4100		0.1				0.0007		1.3		
8/13/2015	10			4100		1				9.3		10		30
10/27/2015	4.8			4200		0.22				5.3		0.93		30

Appendix Table I.1-4
Surface Water Quality - Bedell Pond
White Pine Copper LLC

Detected Analytes											
Date	Lab	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Total Recoverable Copper (µg/L)	Dissolved Copper (µg/L)	pH (Lab)(SU)	Mercury, Low Level (ng/L)	Dissolved Calcium (mg/L)	Total Magnesium (mg/L)	Hardness (mg/L)	Chloride (mg/L)
10/8/2006	Lab - General	170	17	54	30	8.4	1.8			120	<10
1/7/2007	Lab - General	250	4	230	130	7.54	3.3			180	<10
4/1/2007	Lab - General						8.1				
4/8/2007	Lab - General	200	19	270	86	7.56				120	10
7/1/2007	Lab - General						3.1				
7/15/2007	Lab - General	170	8	49	31	8.14				120	13
10/7/2007	Lab - General						7.9				
10/21/2007	Lab - General	190	30	320	99	7.2				120	12
1/6/2008	Lab - General						2.6				
1/27/2008	Lab - General	200	<4	150	110	7.76				140	<10
2/17/2008	Lab - General	180	4	140	110	7.38				130	<10
3/16/2008	Lab - General	160	4	240	160	7.95				110	<10
4/6/2008	Lab - General						3				
4/27/2008	Lab - General	210	24	340	340	7.55				120	<10
5/18/2008	Lab - General	200	18	200	95	8.2				130	<10
6/15/2008	Lab - General	180	6	82	82	8.22				130	<10
7/6/2008	Lab - General						1.5				
10/5/2008	Lab - General						3.1				
10/19/2008	Lab - General	180	13	82	34	8.28				150	<10
1/4/2009	Lab - General						1.5				
1/18/2009	Lab - General	230	13	110	74	7.49				160	<10
4/5/2009	Lab - General						2.9				
4/19/2009	Lab - General	170	9	140	80	8.16				120	<10
7/19/2009	Lab - General	160	13	81	30	8.25				130	<10
10/4/2009	Lab - General						1.8				
10/13/2009	Lab - General	180	<4	96	48	7.76				130	<10
1/12/2010	Lab - General						1.9				
1/19/2010	Lab - General	270	<4	110	82	7.66				190	<10
4/12/2010	Lab - General	280	8	86	63	8.25				200	<10
7/18/2010	Lab - General	290	13	29	22	8.52				160	13
10/5/2010	Lab - General						2.3				
10/18/2010	Lab - General	210	5	38	22	8.01				140	<10
12/5/2010	Lab - General	320	<4	56	43	7.9				170	<10
1/3/2011	Lab - General	250	<4	75	41	7.73				180	<10
1/11/2011	Lab - General						1.4				
2/6/2011	Lab - General	210	<4	71	60	7.59				210	<10
3/6/2011	Lab - General	300	<4	92	65	7.63				190	<10
4/3/2011	Lab - General	230	<4	110	78	7.8				150	<10
8/7/2011	Lab - General	220	37	24	17	8.32				140	<10

Table I.1-4 (continued)

Detected Analytes											
Date	Lab	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Total Recoverable Copper (µg/L)	Dissolved Copper (µg/L)	pH (Lab)(SU)	Mercury, Low Level (ng/L)	Dissolved Calcium (mg/L)	Total Magnesium (mg/L)	Hardness (mg/L)	Chloride (mg/L)
9/4/2011	Lab - General	200	<4	25	24	8.2				140	<10
10/3/2011	Lab - General	220	6	27	5	8.19				140	<10
10/4/2011	Lab - General						2.8				
11/6/2011	Lab - General	250	7	31	25	7.73				150	<10
12/4/2011	Lab - General	300	4	74	50	7.87				190	10
1/2/2012	Lab - General	340	<4	72	56	7.65				230	13
1/10/2012	Lab - General						2.4				
2/5/2012	Lab - General	350	<4	64	55	7.71				220	<10
3/4/2012	Lab - General	320	<4	69	57	7.79				220	<10
4/1/2012	Lab - General	260	10	74	51	8.03				170	<10
5/6/2012	Lab - General	210	5	130	56	7.99				160	<10
7/1/2012	Lab - General	170	<4	48	5	8.27				140	<10
7/2/2012	Lab - General						1.4				
8/5/2012	Lab - General	160	<4	29	19	8.36				130	<10
9/3/2012	Lab - General	120	<4	33	25	7.93				130	<10
10/7/2012	Lab - General	250	<4	31	21	8.3				130	<10
11/4/2012	Lab - General	200	<8	89	47	7.77				140	<10
12/2/2012	Lab - General	230	<4	57	55	7.68				170	<10
1/7/2013	Lab - General	250	<4	63	48	7.56				210	<10
1/10/2013	Lab - General						1.4				
2/3/2013	Lab - General	320	<4	74	55	7.42				200	<10
3/3/2013	Lab - General	290	<4	63	52	7.51				220	<10
4/2/2013	Lab - General						1.5				
4/7/2013	Lab - General	220	<4	100	74	7.45				210	<10
5/5/2013	Lab - General	190	5.5	170	110	7.29				150	<10
6/2/2013	Lab - General	200	12	150	87	7.56				160	<10
8/4/2013	Lab - General	210	7	44	38	8.42				150	<10
9/2/2013	Lab - General	240	4	32	29	8.17				190	<10
10/6/2013	Lab - General	230	<4	30	11	8.18	2.5			160	<10
11/3/2013	Lab - General	230	<4	61	42	8.03				190	<10
12/1/2013	Lab - General	230	<4	71	77	7.84				210	<10
1/7/2014	Lab - General	350	<4	51	5	7.59				270	<10
1/13/2014	Lab - General						1.1				
2/2/2014	Lab - General	320	<4	42	45	7.55				250	<10
4/6/2014	Lab - General	300	4	100	49	7.15				180	<10
4/8/2014	Lab - General						2				
5/4/2014	Lab - General	150	<4	160	97	7.41				110	<10
7/6/2014	Lab - General	170	<8	34	24	8.2				110	<10
7/14/2014	Lab - General						2.1				
8/3/2014	Lab - General	210	<4	29	19	8.09				110	<10
9/7/2014	Lab - General	140	<4	61	47	7.64				100	<10
10/5/2014	Lab - General	110	12	33	24	7.96				120	<10
10/7/2014	Lab - General						2.1				

Table I.1-4 (continued)

Detected Analytes											
Date	Lab	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Total Recoverable Copper (µg/L)	Dissolved Copper (µg/L)	pH (Lab)(SU)	Mercury, Low Level (ng/L)	Dissolved Calcium (mg/L)	Total Magnesium (mg/L)	Hardness (mg/L)	Chloride (mg/L)
10/14/2014	Lab - General	170		25	34		1.16		7.9	130	<7
12/7/2014	Lab - General	240	<4	58	58	7.44				150	<10
1/4/2015	Lab - General		<4	72	62	7.61				150	
1/21/2015	Lab - General						1.3				
2/1/2015	Lab - General	160	<4	58	46	7.64				160	<10
2/25/2015	Lab - General	210		68			1.1		10	160	4
3/1/2015	Lab - General	40	<4	48	43	7.51				150	<10
4/6/2015	Lab - General	150	<4	86	58	7.76	2.5			110	<10
4/30/2015	Lab - General	180		62			1.2		8.1	130	<4
5/3/2015	Lab - General	160	<4	59	38	8.32				160	<10
6/7/2015	Lab - General		<4	46	36	8.21				150	
7/5/2015	Lab - General	200	<4	39	32	8.48				150	<10
8/2/2015	Lab - General	190	<4	33	29	8.45				130	<10
8/13/2015	Lab - General			31					8.7	130	
9/7/2015	Lab - General	180	<4	64	34	7.89		35	7.4	120	<10
10/4/2015	Lab - General	190	<4	20	13	8.04				130	<10
10/26/2015	Lab - General	210		26			0.59		9.9	150	6
11/1/2015	Lab - General	170	<4	28	19	8.01				140	<10
12/6/2015	Lab - General	260	<4	55	40	7.96				180	<10
1/1/2016	Lab - General						1.5				
1/3/2016	Lab - General	210	<4	72	57	7.65				170	<10
2/8/2016	Lab - General	280	<8	64	53	7.55				210	<10
3/6/2016	Lab - General	250	<4	57	49	7.5				200	<10
4/3/2016	Lab - General	180	<4	90	62	7.85	1.5			120	<10
5/1/2016	Lab - General	180	4	71	49	7.99				130	<10
6/5/2016	Lab - General	95	4	38	33	7.65				91	<10
7/4/2016	Lab - General	210	<4	39	33	8.45	0.81			140	<10
8/7/2016	Lab - General	180	<4	29	22	8.79				120	<10
9/5/2016	Lab - General	160	<4	29	18	8.31				150	<10
10/2/2016	Lab - General	150	4	39	26	7.87				130	<10
11/6/2016	Lab - General	210	<4	20	11	8.13				150	<10
12/4/2016	Lab - General	200	<8	33	21	7.71				150	<10
1/2/2017	Lab - General	240	<4	25	19	7.62				190	<10
1/5/2017	Lab - General						2.9				
2/5/2017	Lab - General	240	<4	41	36	7.73				190	<10
3/5/2017	Lab - General	160	<4	81	53	7.41				140	<10
4/3/2017	Lab - General	55	<4	36	17	7.86	1.3			65	<10
5/1/2017	Lab - General	180	<4	130	69	7.95				120	<10
6/4/2017	Lab - General	180	<4	69	52	8.06				130	<10
7/2/2017	Lab - General	180	<4	38	29	8.11	0.93			140	<10
8/6/2017	Lab - General	210	<4	28	22	8.54				120	<10
9/4/2017	Lab - General		<4	26	19						
10/1/2017	Lab - General	190	<4	22	15	7.92				150	<10

Table I.1-4 (continued)

Detected Analytes											
Date	Lab	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Total Recoverable Copper (µg/L)	Dissolved Copper (µg/L)	pH (Lab)(SU)	Mercury, Low Level (ng/L)	Dissolved Calcium (mg/L)	Total Magnesium (mg/L)	Hardness (mg/L)	Chloride (mg/L)
10/8/2017	Lab - General						0.98				
11/5/2017	Lab - General	180	<4	47	33	7.96				140	<10
12/3/2017	Lab - General	240	<4	38	30	7.87				170	<10
1/1/2018	Lab - General	250	<4	41	29	7.4	0.55			200	<10
2/4/2018	Lab - General		<4	34	27						<10
3/5/2018	Lab - General	300	<4	35	26	7.49				210	<10
4/2/2018	Lab - General	240	<4	48	36	7.55	0.84			190	<10
5/7/2018	Lab - General	180	<4	66	38	7.9				150	<10
6/3/2018	Lab - General		<4	33	23						<10
7/10/2018	Lab - General	160	6	41	29	8.19	1.9			130	<10
8/5/2018	Lab - General	150	<4	26	23	8.55		37	8.9	130	<10
10/7/2018	Lab - General	190	<4	22	12	7.94				150	<10
11/4/2018	Lab - General	210	<4	41	30	7.82		49	9.9	160	<10
12/2/2018	Lab - General	280	<4	39	34	7.69				200	<10
1/6/2019	Lab - General	280	4	36	31	7.39	0.54			230	<10
2/3/2019	Lab - General	10	<4	29	29	6.99		74	15	250	<10
3/4/2019	Lab - General	320	<4		26	7.5				240	<10
4/8/2019	Lab - General	89	6	120	70	7.06	4.4			72	<10
5/6/2019	Lab - General	170	6	83	46	8				110	<10
6/2/2019	Lab - General	170	<4	62	42	7.72		35		120	<10
7/7/2019	Lab - General	170	<4	29	23	8.57	0.2			130	<10
8/4/2019	Lab - General	140	<4	26	18	8.9				110	<10
9/2/2019	Lab - General	170	<4	23	14	7.85				120	<10
10/6/2019	Lab - General	170	4	30	17	7.99	0.74			130	<10
11/3/2019	Lab - General	180	<4	26	18	7.88				160	<10
12/1/2019	Lab - General	230	<4	32	27	7.84				180	<10
1/5/2020	Lab - General	210	<4	50	42	7.64	1.3			160	<10
2/2/2020	Lab - General	200	<4	42	36	7.43				180	<10
3/2/2020	Lab - General	120	<4	30	30	7.7				190	<10
4/6/2020	Lab - General	75	<9.1	62	53	7.84	1.4			120	<10
5/4/2020	Lab - General	170	<4	47	40	7.88				140	<10
6/1/2020	Lab - General	120	<4	87	60					110	<10
7/5/2020	Lab - General	140	<4	28	22	8.3	0.66			120	<10
8/2/2020	Lab - General	150	<4	19	16	8.51				100	<10
9/7/2020	Lab - General	96		15	12					120	
10/4/2020	Lab - General	76	<4	17	11	7.41	0.5			130	<10
11/1/2020	Lab - General	220	<4	20	16	7.97				150	<10
12/6/2020	Lab - General	240	<4	20	17	7.94				160	<10
1/3/2021	Lab - General	260	<4	19	17	7.77	0.5			210	<10
1/3/2021	Trace	260	<4	19	17	7.88				210	<10
1/3/2021	Trace						<0.5				
2/8/2021	Lab - General	250	<4	18	16	7.46				200	<10
2/8/2021	Trace	250	<4	18	16	7.46				200	<10

Table I.1-4 (continued)

Detected Analytes											
Date	Lab	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Total Recoverable Copper (µg/L)	Dissolved Copper (µg/L)	pH (Lab)(SU)	Mercury, Low Level (ng/L)	Dissolved Calcium (mg/L)	Total Magnesium (mg/L)	Hardness (mg/L)	Chloride (mg/L)
3/8/2021	Lab - General	210	<4		16	7.49				200	<10
3/8/2021	Trace	210	<4		16	7.49				200	<10
4/4/2021	Lab - General	150	<4	36	26	7.66	1.2			140	<10
4/4/2021	Trace	150	<4	36	26	7.66	1.2			140	<10
5/3/2021	Lab - General	200	<4	27	30	8.04				170	<10
5/3/2021	Trace	200	<4	27	20	8.04				170	<10
6/7/2021	Lab - General	230	<4	14	13	8.51				160	<10
6/7/2021	Trace	230	<4	14	13	8.51				160	<10
7/5/2021	Lab - General	180	<4	18	14	8.8				130	<10
7/5/2021	Trace	180	<4	18	14	8.8	0.54			130	<10
8/1/2021	Lab - General	170	4	13	10	8.88				110	<10
8/1/2021	Trace	170	4	13	9.8	8.88				110	<10
9/6/2021	Lab - General	170	4	15	9					130	<10
9/6/2021	Trace	170	<4	15	8.8					130	<10
10/3/2021	Lab - General	190	<4	17	12	7.81				140	<10
10/3/2021	Trace	190	<4	17	12	7.81	0.55			140	<10
11/7/2021	Lab - General	240	<4	18	13	7.96				180	<10
11/7/2021	Trace	240	<4	18	13	7.96				180	<10
12/5/2021	Lab - General	200	<4	21	16	7.68				200	<10
12/5/2021	Trace	200	<4	21	16	7.68				200	<10
1/2/2022	Lab - General	230	<4	37	28	7.2				200	<10
1/2/2022	Trace	230	<4	37	28	7.2	0.86			200	<10
2/6/2022	Lab - General	190	<4	24	22	7.11				200	<10
2/6/2022	Trace	190	<4	24	22	7.11				200	<10
3/7/2022	Lab - General	270	<4	22	18	7.48				220	<10
3/7/2022	Trace	270	<4	22	18	7.48				220	<10
4/3/2022	Lab - General	180	<4	44	37	6.96	1.3			160	<10
4/3/2022	Trace	220	<4	44	37	6.96	1.3			160	<10
5/2/2022	Lab - General	180	<4	43	26	6.74				120	<10
5/2/2022	Trace	180	<4	43	26	6.74				120	<10
6/6/2022	Lab - General	200	4	30	25	7.98				150	<10
6/6/2022	Trace	200	4	30	25	7.98				150	<10
7/3/2022	Trace	150	<4	28	24	8.45	1.1			110	<10
8/7/2022	Trace	160	4	26	21	7.8				110	<10
9/5/2022	Trace	220	<4			8.32				110	<10
10/2/2022	Trace	220	<4	15	13	7.61	<0.5			150	<10
11/6/2022	Trace	180	<4	16	13	7.9				140	<10
12/4/2022	Trace	200	<4	34	24	7.15				160	<10
1/2/2023	Trace	110	<4	26	27	6.73				180	<10
2/5/2023	Trace	360	<4	28	22	7.43				210	<10
3/6/2023	Trace	270	<4	28	22	7.46				200	<10
4/3/2023	Trace	170	<4	58	21	7.48				200	<10
4/19/2023	Trace	80		67	52						

Table I.1-4 (continued)

Detected Analytes											
Date	Lab	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Total Recoverable Copper (µg/L)	Dissolved Copper (µg/L)	pH (Lab)(SU)	Mercury, Low Level (ng/L)	Dissolved Calcium (mg/L)	Total Magnesium (mg/L)	Hardness (mg/L)	Chloride (mg/L)
4/19/2023	Trace	80	<4	67	52						
5/1/2023	Trace	150	<4	54	2.2	7.82				120	<10
6/5/2023	Trace	190	<4	26	20	7.86				140	<10
7/4/2023	Trace	130	<4	24	19	8.34	1.7			120	<10
7/17/2023	Trace	120	<4	17	14						
8/6/2023	Trace	190	<4	16	13	8.74				110	<10
8/26/2023	Trace	120	<4	19	13						
9/4/2023	Trace	140	<4	14	12	8.65				98	<10
9/12/2023	Trace			7.9	11						
9/12/2023	Trace	140	<4								
10/1/2023	Trace	160	<4	12	10	7.58	<0.5			120	<10
10/17/2023	Trace			10	9.2						
10/17/2023	Trace	160	<4								
11/5/2023	Trace	190	<4	16	12	7.55				150	<10
11/20/2023	Trace	200	<4	19	12						
12/3/2023	Trace	230	<4	17	15	7.7				180	<10
12/20/2023	Trace	220	<4	22	20						
1/7/2024	Trace	240	<4	19	19	7.72	0.5			170	<10
2/4/2024	Trace	190	<4	19	15	7.44				200	<10
3/4/2024	Trace	140	<4	23	18	7.57				160	<10
3/23/2024	Trace	220	<4	20	13						
4/8/2024	Trace	220	<4	26	21	7.9				140	<10
4/18/2024	Trace	140	<4	25	20						
5/6/2024	Trace	190	<4	24	18	8.06				170	<10
5/19/2024	Trace	210	<4	22	13						
6/2/2024	Trace	380	<4	20	14	8.16				150	<10
6/20/2024	Trace	200	<4	24	24						

Notes

Prepared by: KRM2, LDC

- Blank cells represent an analyte not tested during that event.

Checked by: DCF1

- Significant figures are as reported from the database obtained from White Pine Copper.

mg/L = milligram per liter

µg/L = microgram per liter

ng/L = nanogram per liter

Appendix Table I.1-4a
Surface Water Quality - Bedell Pond
White Pine Copper LLC

Detected Analytes										
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Total Recoverable Copper (µg/L)	Dissolved Copper (µg/L)	pH (Lab)(SU)	Mercury, Low Level (ng/L)	Dissolved Calcium (mg/L)	Total Magnesium (mg/L)	Hardness (mg/L)	Chloride (mg/L)
7/7/2024	120	<4.1	27	25	8.54	0.66			110	<10
7/17/2024	190	<4	21	19						
8/3/2024	150	<4	18	15	8.75				110	<10
8/26/2024	140	<5.7	17	13						
9/3/2024	160	<4	21	14	8.03				120	<10
9/25/2024	170	<4.1	19	13						
10/16/2024	150	<4	21	14						
10/16/2024	170	<4	21	15						
10/28/2024	180	<4.1	19	13	8.02				150	<10
11/4/2024	190	<4.1	22	18	7.94	0.61			130	<10
11/4/2024						<0.2				
11/18/2024	190	<4	23	15						
12/1/2024	210	<4	23	18	7.96				160	<10
1/5/2025	230	<4	28	22	7.7	0.66			160	<10
2/2/2025	250	<4	27	22	7.56				190	<10
3/3/2025	240	<4	36	27	7.68				170	<10
4/7/2025	180	<4	41	32	7.57	1.2			140	<10
5/5/2025	200	<4	47	29	7.77				120	<10
5/20/2025	160	<4.1	25	14						
6/2/2025	<21	<4	15	10	8.28				160	<10
6/17/2025	200	<4	15	8.8						
7/24/2025	150	<4	30	23						
8/3/2025	150	<4	24	18	8.3				120	<10
9/1/2025	150	<4	14	13	8.21				110	<10
10/5/2025	180	<4.1	18	11	8.11	<0.5			140	<10
10/15/2025	170	<4	17	9.4						
11/2/2025	210	4.1	19	11	8.11				160	<10
12/7/2025	210	<4	18	16	7.85				160	<10
1/4/2026	250	<4	25	20	7.59	<0.5			200	<10
2/1/2026	270	<4	24	27	7.52				190	<10
3/1/2026	260	<4.1	23	21	7.45				200	<10
4/5/2026	200	<4	38	29	7.83	0.6			160	<10
5/4/2026	180	4	40	22	8.04				130	<10
6/1/2026	180	<4	21	11	8.65				140	<10

Notes

Prepared by: KRM2, LDC

Checked by: DCF1

1. Blank cells represent an analyte not tested during that event.

2. Significant figures are as reported from the database obtained from White Pine Copper.

mg/L = milligram per liter

µg/L = microgram per liter

ng/L = nanogram per liter

Appendix Table I.1-5
Surface Water Quality - Biotic Ligand Model Sample
White Pine Copper LLC

Detected Analytes										
Date	Dissolved Organic Carbon (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Dissolved Calcium (mg/L)	Dissolved Magnesium (mg/L)	pH (Lab)(SU)	Dissolved Potassium (mg/L)	Dissolved Sodium (mg/L)	Temperature Field (°F)	Total Alkalinity as CaCO3 at pH of 4.5 (mg/L)
1/3/2021	5.1	47	330	110	14	7.06	8.3	110	33	120
2/8/2021	4.9	110	400	130	16	6.97	<10	120	33	130
3/8/2021	5.2	56	540	130	17	7.11	9.8	120	33	140
4/4/2021	4	23	120	46	6	7.32	4.1	40	41	80
5/3/2021	3.7	32	170	72	7.3	7.23	4.9	55	53	99
6/7/2021	4.1	28	200	79	9.4	7.55	5.3	64	75	100
7/5/2021	4.2	26	200	71	9.7	7.76	4.6	81	81	70
8/1/2021	4.2	26	210	75	9.9	7.18	5.2	84	75	65
9/6/2021	4.4	22	210	76	12	7.04	6.7	78	67	85
10/3/2021	4.2	24	200	73	11	7.8	6.1	71	67	87
11/7/2021	4.1	24	220	76	12	8.07	5.6	77	44	95
12/5/2021	4.5	46	340	120	17	7.61	7.3	130	34	110
1/4/2022	4.4	50	340	110	13	7.45	8.1	120	33	97
2/6/2022	5.1	50	360	120	15	7.29	8.1	100	33	120
3/7/2022	5.1	52	810	150	21	7.01	7.9	130	33	140
4/3/2022	4.8	22	82	56	8.1	7.43	4.6	33	1.11	110
5/2/2022	3.4	12	58	41	4.8	7.33	3.1	25	46	76
6/6/2022	4	16	91	53	6.8	7.34	3.5	26	66	110
7/3/2022	4.2	14	81	53	7.5	7.53	2.7	27		95
8/7/2022	4.4	12	95	51	8.5	6.93	2.9	34		84
9/5/2022	4.2	12	110	55	8.2	7.18	3.2	34		98
10/2/2022	4.3	<15	110	58	8.6	7.27	3.5	36		98
11/6/2022	4	24	150	67	10	7.61	4.4	50		96
12/4/2022	4.3	23	120	59	7.5	7.11	4.1	45		86
1/2/2023	5.1	35	130	70	9.8	6.95	4.9	48		100
2/5/2023	6.3	27	130	83	11	7.01	5.5	48		140
3/6/2023	5.5	30	150	92	10	7.15	5.6	50		170
4/3/2023	4.6	22	130	82	11	7.4	6.1	50		160
5/1/2023	3.1	<15	65	40	4.2	7.29	2.4	22		92
6/5/2023	3.9	<15	77	58	6.7	7.57	<10	25		100
7/4/2023	3.5	12	92	48	7.7	8.13	2.8	36		75
8/6/2023	3.5	<15	100	41	8.1	8.06	3.1	37		54
9/4/2023	4	<15	120	55	9.9	7.53	4	42		77
10/1/2023	4.3	15	130	61	11	7.37	4.6	35		84
11/5/2023	4.1	16	130	65	13	7.67	5.6	40		91
12/3/2023	4.7	40	200	100	19	7.6	6.9	43		110
1/7/2024	3.4	30	200	72	11	7.23	5.2	68		95
2/4/2024	3.8	32	240	88	2.5	7.34	<1	15		110
3/4/2024	4.1	34	210	79	10	7.36	5.4	80		110
4/8/2024	3.9	43	220	89	9.8	7.62	5.5	110		87
5/6/2024	4	44	260	92	10	7.62	5.2	98		97
5/15/2024	4.7	44	250	90	10	7.75	5.3	99		100
6/2/2024	4.4	42	250	87	11	8.21	4.8	94		46
7/7/2024	4.9	32	200	66	9.1	7.96	3.8	81		68
8/3/2024	5.1	26	230	61	9.3	8.01	3.4	76		70
9/3/2024	6.1	26	220	79	12	7.98	4.7	87		93
10/28/2024	6.1	21	230	84	13	7.6	5.1	82		100
11/4/2024	6.4	36	240	97	17	7.28	5.8	77	49	110
12/1/2024	4.6	30	190	73	11	7.84	5.1	70	33	96

Notes:

mg/L = milligram per liter

µg/L = microgram per liter

Blank cells represent an analyte not tested during that event.

Prepared by: KRM2, LDC

Checked by: DCF1

Appendix Table I.1-5a
Surface Water Quality - Biotic Ligand Model Sample
White Pine Copper LLC

Detected Analytes										
Date	Dissolved Organic Carbon (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Dissolved Calcium (mg/L)	Dissolved Magnesium (mg/L)	pH (Lab)(SU)	Dissolved Potassium (mg/L)	Dissolved Sodium (mg/L)	Temperature Field (°F)	Total Alkalinity as CaCO3 at pH of 4.5 (mg/L)
7/7/2024	4.9	32	200	66	9.1	7.96	3.8	81		68
8/3/2024	5.1	26	230	61	9.3	8.01	3.4	76		70
9/3/2024	6.1	26	220	79	12	7.98	4.7	87		93
10/28/2024	6.1	21	230	84	13	7.60	5.1	82		100
11/4/2024	6.4	36	240	97	17	7.28	5.8	77	49	110
12/1/2024	4.6	30	190	73	11	7.84	5.1	70	33	96
1/5/2025	5.4	23	110	67	9.5	7.96	4.8	44	32	110
2/2/2025	5.5	26	110	64	10	7.74	4.5	36	33	130
3/3/2025	5.9	23	140	76	11	7.63	4.2	38	0.56	150
4/7/2025	3.9	<15	38	38	4.9	7.89	2.7	13	37	80
5/5/2025	4	16	70	48	5.6	7.78	3.5	28	55	87
6/2/2025	4.5	19	110	68	8.9	8.05	4	35	68	110
7/6/2025	4.7	20	130	54	10	7.17	3.1	35	78	68
8/3/2025	5.2	17	140	59	10	7.11	3.4	46	75	75
9/1/2025	5.1	15	160	61	10	7.5	3.8	45	21.7	94
10/5/2025	5.1	22	190	79	14	7.69	4.6	52	67	140
11/2/2025	4.6	23	220	71	13	8.16	3.8	52	44	110
11/16/2025	4.8	25	250	92	16	7.94	5.1	67	40	120
12/7/2025	4.1	29	260	76	11	7.07	4.9	83	33	93
1/4/2026	5.5	37	270	88	13	7.44	6.2	90	33	120
2/1/2026	6.4	37	240	84	13	7.38	5.5	75	33	150
3/1/2026	6.7	35	260	97	13	7.35	5	76	33	160
4/5/2026	5	<15	46	46	6.9	7.52	3.7	18	35	110
5/4/2026	3.9	<15	58	37	4.2	7.32	2.6	19	53	80
6/1/2026	4.5	<15	83	48	6.2	7.72	2.8	22	69	100

Notes:

mg/L = milligram per liter

µg/L = microgram per liter

Blank cells represent an analyte not tested during that event.

Prepared by: KRM2, LDC

Checked by: DCF1

Appendix Table I.1-6
Surface Water Quality - Culvert - Historical
White Pine Copper LLC

Detected Analytes					
Date	Lab	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Chloride (mg/L)
1/8/2006	Lab - General	<4	25	34	
2/12/2006	Lab - General	<4	38	46	
3/12/2006	Lab - General	9	24	39	
4/9/2006	Lab - General	5	41	12	
5/7/2006	Lab - General	15	42	13	
6/11/2006	Lab - General	8	34	57	
7/9/2006	Lab - General	8	16	31	
11/12/2006	Lab - General	5	86	17	
12/10/2006	Lab - General	<4	15	19	
1/14/2007	Lab - General	<4	23	31	
3/11/2007	Lab - General	<4	22	25	
4/8/2007	Lab - General	14	65	220	
5/13/2007	Lab - General	5	32	59	
6/10/2007	Lab - General	5	25	41	
7/8/2007	Lab - General	<4	18	20	
10/14/2007	Lab - General	8	24	67	
2/9/2008	Lab - General	<4	58	61	
4/13/2008	Lab - General	7	48	74	
5/11/2008	Lab - General	25	40	160	
4/12/2009	Lab - General	<4	41	85	
5/10/2009	Lab - General	14	35	81	
6/14/2009	Lab - General	4	14	19	
10/11/2009	Lab - General	6	11	30	
11/8/2009	Lab - General	12	32	66	
2/14/2010	Lab - General	<4	36	41	
3/14/2010	Lab - General	<4	41	40	
4/11/2010	Lab - General	5.3	33	54	
5/9/2010	Lab - General	5.3	18	26	
7/11/2010	Lab - General	11	15	26	
8/8/2010	Lab - General	<4	9.6	21	
9/12/2010	Lab - General	<4	5.2	400	
10/10/2010	Lab - General	5	11	14	
11/14/2010	Lab - General	<4	16	19	
12/12/2010	Lab - General	<4	16	19	
1/9/2011	Lab - General	<4	31	32	
5/8/2011	Lab - General	6	36	75	
6/12/2011	Lab - General	6	36	67	
7/10/2011	Lab - General	<4	24	30	
8/14/2011	Lab - General	4	7	10	
10/9/2011	Lab - General	<4	5.2	8.1	
11/13/2011	Lab - General	7	12	17	
4/8/2012	Lab - General	6	3.5	5.4	
7/8/2012	Lab - General	<4	19	22	
8/12/2012	Lab - General	<4	18	24	
9/9/2012	Lab - General	<4	8	11	
10/14/2012	Lab - General	8	12	19	
11/11/2012	Lab - General	7	26	68	
12/9/2012	Lab - General	<4	29	42	
5/12/2013	Lab - General	24	79	180	
6/9/2013	Lab - General	8	42	68	
7/14/2013	Lab - General	<4	26	41	
8/11/2013	Lab - General	<4	17	22	
9/8/2013	Lab - General	9	5.2	9.7	

Table I.1-6 (continued)

Detected Analytes					
Date	Lab	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Chloride (mg/L)
10/13/2013	Lab - General	<4	18	170	
11/10/2013	Lab - General	34	28	89	
4/1/2014	Lab - General	9	42	86	
5/11/2014	Lab - General	26	79	220	
6/8/2014	Lab - General	12	36	62	
7/13/2014	Lab - General	<4	19	9.9	
8/10/2014	Lab - General	<4	15	26	
9/14/2014	Lab - General	12	90	71	
10/12/2014	Lab - General	6	29	46	
11/9/2014	Lab - General	15	32	59	
4/12/2015	Lab - General	8	35	56	
5/10/2015	Lab - General	5	30	41	
6/14/2015	Lab - General	<4	21	26	
7/12/2015	Lab - General	<4	16	20	
8/9/2015	Lab - General	6	11	14	
9/13/2015	Lab - General	<4	15	25	
10/11/2015	Lab - General	<4	11	13	
11/8/2015	Lab - General	7	20	41	
12/13/2015	Lab - General	5	35	55	
3/13/2016	Lab - General	<4	32	36	120
4/10/2016	Lab - General	<4	27	42	94
5/8/2016	Lab - General	<4	24	42	140
6/12/2016	Lab - General	<4	18	30	160
7/20/2016	Lab - General	4	17	26	240
8/14/2016	Lab - General	<4	15	27	
9/11/2016	Lab - General	<4	24	37	190
10/9/2016	Lab - General	5	14	27	220
11/13/2016	Lab - General	<4	21	49	260
4/9/2017	Lab - General	<4	19	31	170
5/8/2017	Lab - General	5	34	68	120
6/11/2017	Lab - General	10	34	61	150
7/9/2017	Lab - General	4	17	25	150
8/13/2017	Lab - General	<4		21	190
9/10/2017	Lab - General	<8	20	32	190
10/8/2017	Lab - General	<4	18	26	220
5/13/2018	Lab - General	<4	19	41	120
6/10/2018	Lab - General	<4	15	23	200
7/8/2018	Lab - General	<4	13	21	200
8/12/2018	Lab - General	<4	12	16	260
9/9/2018	Lab - General	8	10	18	
10/14/2018	Lab - General	14	28	59	
11/11/2018	Lab - General	7	26	52	150
12/9/2018	Lab - General	5	39	39	160
1/13/2019	Lab - General	<4	31	32	91
4/15/2019	Lab - General	<4	55	54	26
5/13/2019	Lab - General	7	30	61	86
6/9/2019	Lab - General	4	26	38	120
7/14/2019	Lab - General	8	10	13	160
8/11/2019	Lab - General	<4	6.6	13	210
10/13/2019	Lab - General	<4	15	27	210
4/13/2020	Lab - General	11	21	40	110
5/11/2020	Lab - General	<4	19	36	110
6/7/2020	Lab - General	4	17	24	140
7/12/2020	Lab - General	<4	15	19	180
8/9/2020	Lab - General	<4	7.5	10	160
9/13/2020	Lab - General	<4	8.5	12	330
10/11/2020	Lab - General	4	11	15	280

Table I.1-6 (continued)

Detected Analytes					
Date	Lab	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Chloride (mg/L)
11/8/2020	Lab - General	13	20	41	300
12/13/2020	Lab - General	<4	21	28	320
3/14/2021	Lab - General	<4	32	38	220
3/14/2021	Trace	<4	32	38	220
4/12/2021	Lab - General	7	20	48	130
4/12/2021	Trace	7	20	48	130
5/10/2021	Lab - General	<4	18	28	180
5/10/2021	Trace	<4	18	28	180
6/14/2021	Lab - General	4	12	16	220
6/14/2021	Trace	4	12	16	220
7/11/2021	Lab - General	<4	5.7	10	180
7/11/2021	Trace	<4	5.7	10	180
8/8/2021	Lab - General	4	1.5	2.2	94
8/8/2021	Trace	4	1.5	2.2	94
11/14/2021	Lab - General	<4	6.5	11	36
11/14/2021	Trace	<4	6.5	11	36
4/11/2022	Lab - General	14	37	67	27
4/11/2022	Trace	14	37	67	27
5/9/2022	Lab - General	4	24	50	78
5/9/2022	Trace	4	24	50	78
6/13/2022	Lab - General	<4	25	38	81
6/13/2022	Trace	<4	25	38	81
7/11/2022	Trace	<4	18	23	81
8/14/2022	Trace	<4	17	20	110
9/12/2022	Trace	<4	10	9.1	120
10/9/2022	Trace	<4	1.7	1.8	58
11/13/2022	Trace	11	25	63	110
12/11/2022	Trace	<4	30	39	110
4/9/2023	Trace	<4	29	34	150
5/8/2023	Trace	7.9	21	45	61
6/11/2023	Trace	<4	12	19	120
7/9/2023	Trace	<4	12	17	120
11/12/2023	Trace	<4	9.1	18	310
12/10/2023	Trace	<4	8.2	13	270
2/11/2024	Trace	10	18	43	220
3/11/2024	Trace	<4	23	19	210
4/15/2024	Trace	<4	21	26	280
5/13/2024	Trace	5	18	29	270
6/9/2024	Trace	<4	14	24	270

Notes:

Prepared by: KRM2, LDC

Checked by: DCF1

1. Sample taken 8/13/2017 for Total Dissolved Solids (580 mg/L) was excluded from the table due to lack of data.

2. Blank cells represent an analyte not tested during that event.

3. Significant figures are as reported from the database obtained from White Pine Copper.

mg/L = milligram per liter

µg/L = microgram per liter

ng/L = nanogram per liter

Appendix Table I.1-6a
Surface Water Quality - Culvert - Baseline
White Pine Copper LLC

Detected Analytes				
Date	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Chloride (mg/L)
7/14/2024	<4	23	26	220
8/11/2024	<4	7.9	12	320
9/10/2024	<4.1	6.6	7.3	290
10/15/2024	<4	9.8	16	200
11/12/2024	8.1	18	47	190
12/9/2024	<4	20	31	190
3/10/2025	<4	24	37	97
4/13/2025	<4	24	42	45
5/12/2025	4	26	48	87
6/8/2025	5.1	12	17	170
7/13/2025	<4	13	19	160
8/10/2025	<4	5	16	140
9/7/2025	<4	9	13	230
10/12/2025	<4	9.5	10	200
11/9/2025	4.1	9.9	12	310
12/14/2025	<4.2	20	22	270
1/11/2026	<4.1	30	40	230
2/8/2026	5	27	34	240
3/9/2026	4	34	44	170
4/13/2026	5.2	21	30	43
5/12/2026	7.7	19	48	78
6/7/2026	4.4	17	25	220

Notes:

Prepared by: KRM2, LDC

1. Blank cells represent an analyte not tested during that event.

Checked by: DCF1

2. Significant figures are as reported from the database obtained from White Pine Copper.

mg/L = milligram per liter

µg/L = microgram per liter

Appendix Table I.1-7
Surface Water Quality - Perch Creek Outfall (001A)
White Pine Copper LLC

Detected Analytes																			
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Total Silver (µg/L)	Dissolved Silver (µg/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)	Total Arsenic (µg/L)	Total Cadmium (µg/L)	Dissolved Cadmium (µg/L)	Conductivity (Field) (µS/cm)	Chloride (mg/L)	Hardness (mg/L)	Total Lithium (µg/L)	Low Level Mercury (ng/L)	Total Selenium (µg/L)	Dissolved Strontium (µg/L)	Temperature (°F)
1/7/1998	780	2		33									321	395					35
1/13/1998	750	1		22									308	415	44				32
1/21/1998	820			29									305	420					34
1/28/1998	940			24									317	455					35
2/4/1998	970			18									280	470					34
2/11/1998	840	1		21							2		270	460	42				34
2/18/1998	1100			26									270	470					36
2/25/1998	820			35									210	340					35
3/4/1998	550			140							0.3		150						
3/11/1998	530	12		120									140	230	29				
3/18/1998	520	10		130									130	250					
3/25/1998	580	9		60							0.2		120	250					
4/1/1998	410	86		400							0.3		82	190					
4/8/1998	360	10		60									93	190					
4/15/1998	470			31									100	210	24				
4/22/1998	440	6		21									130	280					
4/29/1998	750	5		24									160	310					
5/6/1998	560	8		17									120	230					
5/12/1998	640	5		16									140	240	30				
5/20/1998	660	2		12									160	280					
5/27/1998	730	4		14							0.7		180	290					
6/3/1998	700	4		14							0.6		190	300					
6/10/1998	690	2		19									170	270	38				
6/17/1998	940	10		21									210	340					
6/24/1998	610	3		18									240	320					
7/1/1998	960	1		15									190	290					
7/8/1998	1000	2		13									210	310	38				
7/15/1998	940	3		20							0.3		230	310					
7/22/1998	840	4		18									220	330					
7/29/1998	960	2		17									210	340					
8/5/1998	870	3		17									240	340					
8/12/1998	970	3		17							0.2		240	340	41				
8/19/1998	660	6		22							0.4		260	360					
8/26/1998	820	4		18							0.6		220	340					
9/2/1998	890	4		19							0.3		220	310					
9/9/1998	860	2		16									220	340	60				
9/16/1998	920	2		17							0.6		210	310					
9/23/1998	750	2		29									210	310					
9/30/1998	700	1		11									230	340					
10/7/1998	470	6		15							0.8		210	290					
10/14/1998	700	4		22									230	290	30				
10/21/1998	720	7		18							1.1		220	290					
10/28/1998	1100	4		20									230	310					
11/4/1998	900	5		18									120	280					
11/11/1998	680	4		17									270	320	39				
11/18/1998	610	10		46									230	310					
11/24/1998	720	30		15									220	340					
12/2/1998	610	14		49									230	330					
12/9/1998	640	9		79									250	330	42				
12/16/1998	670	6		140									270	310					
12/22/1998	680	4		33									260	360					
12/29/1998	720	2		31									280	450					
1/6/1999	780	2		28							<0.2		310	420					32
1/13/1999	870	5		30		<0.2					<0.2		290	450		<0.2			32
1/20/1999	880	1		35							<0.2		320	450					33
1/27/1999	940	4		27							<0.2		340	490					33
2/3/1999	880	4		37							<0.2		330			<0.2			33
2/10/1999	1000	4		28		<0.2					<0.2		330		55	<0.2			
2/16/1999	760	5		35							<0.2		280						
2/24/1999	900	4		48		<0.2					<0.2		280						
3/3/1999	940	9		51							<0.2		400			<0.2			
3/10/1999	1100	9		74		<0.2					<0.2		440		59	<0.2			
3/17/1999	940	4		74							0.3		330						
3/25/1999	780	6		24							0.3		280						
3/31/1999	690	20		110							<0.3		190						
4/7/1999	490	24		170							<0.2		140			<0.2			
4/14/1999	450	12		58		<0.2					<0.2		150		23	<0.2			
4/21/1999	450	8		49							<0.2		150						
4/28/1999	570	10		90							<0.2		39						
5/5/1999	530	11		62		<0.2					<0.2		160		28	<0.2			
5/12/1999	650	5		42							<0.2		160			<0.2			
5/19/1999	600	5		32							<0.2		150						
5/26/1999	660	10		49							<0.2		160						
6/2/1999	680	5		25							<0.2		160	270		<0.2			55
6/9/1999	920	28		19		<0.2					<0.2		290	390	30	<0.2			71
6/16/1999	560	6		56							<0.2		150	240					65
6/23/1999	670	3		19							<0.2		180	230					71
6/30/1999	730	2		23							0.45		180	280					69
7/7/1999	710	3		24							0.23		170	260		<0.2			74
7/14/1999	690	3		22		<0.2					<0.2		150	240	31	<0.2			71
7/21/1999	670	4		16							<0.2		170	230					75
7/28/1999	730	3		20							<0.2		180	250					76
8/4/1999	790	2		31		<0.2					<0.2		190	280		<0.2			74
8/11/1999	740	2		19		<0.2					<0.2		210	280	40	<0.2			69
8/18/1999	900	4		30							<0.2		210	340					68
8/25/1999	870	3		16							<0.2		210	300					73
9/1/1999	590	4		23		<0.2					<0.2		210	300		<0.2			68
9/8/1999	870	4		17		<0.2					<0.2		220	320	36	<0.2			67
9/15/1999	800	4		32							<0.2		210	270					59
9/22/1999	830	5		43							<0.2		240	330					51
9/29/1999	830	5		25							<0.2		220	360					57
10/6/1999	870	12		16							<0.2		240	360					45

Table I.1-7 (continued)

Detected Analytes																			
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Total Silver (µg/L)	Dissolved Silver (µg/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)	Total Arsenic (µg/L)	Total Cadmium (µg/L)	Dissolved Cadmium (µg/L)	Conductivity (Field) (µS/cm)	Chloride (mg/L)	Hardness (mg/L)	Total Lithium (µg/L)	Low Level Mercury (ng/L)	Total Selenium (µg/L)	Dissolved Strontium (µg/L)	Temperature (°F)
10/13/1999	880	4		32		<0.2					<0.2		230	390	43	<0.2			51
10/20/1999	880			12							<0.2		230	400					44
10/27/1999	930			44							<0.2		260	400					40
11/3/1999	700	15		48							<0.2		130	290	37	<0.2			42
11/10/1999	690			41							<0.2		lab error	350					44
11/17/1999	750	8		41							<0.2		220	350		<0.2			40
11/24/1999	730			34							<0.2		240	320					42
12/1/1999	720	18		52							<0.2		230	390	36	<0.2			35
12/8/1999	690			45							<0.2		220	370					35
12/15/1999	530	10		43							<0.2		230	370		<0.2			37
12/22/1999	700			42							<0.2		240	400					36
12/29/1999	320			41							<0.2		240	370					35
1/6/2000	800	18		35							2.3		260	410	35	<0.2			35
1/12/2000	850			33		<0.2					<0.2		270	420					36
1/19/2000	800	12		33							<0.2		280	500		<0.2			35
1/25/2000	980			28							<0.2		290	480					28
2/2/2000	990	17		32							<0.2		320	500	42	<0.2			34
2/9/2000	890			35							<0.2		330	530					35
2/16/2000	930			33							<0.2		330	540		<0.2			34
2/23/2000	1000			36							<0.2		320	540					35
3/1/2000	440			82							<0.2		160	270	27	<0.2			37
3/8/2000	370	12		93							<0.2		120	230					44
3/15/2000	470			100							<0.2		110	210		<0.2			36
3/22/2000	450			67							2.2		110	230					40
3/29/2000	440			200							<0.2		93	200					40
4/5/2000	400	21		84							<0.2		95	210	<0.02	<0.2			42
4/12/2000	370			75		<0.2					<0.2		100	220					44
4/19/2000	580		28	52							<0.2		110	230		<0.2			43
4/26/2000	420		26	52							<0.2		120	250					53
5/3/2000	560	15	31	41							<0.2		130	270		<0.2			56
5/10/2000	650	16	21	28							<0.2		140	290					61
5/17/2000	660		26	22							<0.2		150	300		<0.2			59
5/24/2000	770	11	22	22							<0.2		160	330					62
5/31/2000	770		15	18							<0.2		160	320					62
6/7/2000	650		16	15							<0.5		170	280		<0.2			63
6/14/2000	580	12	12	21							<0.5		170	270					67
6/21/2000	720		17	18							<0.5		230	340		<0.2			67
6/28/2000	770		18	33							<0.2		200	260					69
7/6/2000	580		15	18							<0.2		170	300		<0.2			71
7/12/2000	630		15	35		<0.2					<0.2		160	280	<0.25				73
7/19/2000	660		10	14							<0.2		160	290		<0.2			66
7/26/2000	660		19	12							<0.2		170	290					75
8/2/2000	670		12	11									170	290					75
8/9/2000	500	20	16	11									180	300					65
8/16/2000	770		12	16									180	310					67
8/23/2000	750			13									190	330					65
8/30/2000	630			14									170	320					63
9/6/2000	650	11	10	16							0.2		200	330					59
9/13/2000	740		10	14									190	310					58
9/20/2000	700			10									200	340					54
9/27/2000	730			11									200	350					54
10/4/2000	650			9									200	340					52
10/11/2000	810			10		<0.2					0.3		210	350					43
10/18/2000	580			9									210	360					49
10/25/2000	660		14	27									210	360					58
11/1/2000	680			11									210	360					51
11/8/2000	710			14									210	370					44
11/14/2000	740			11									220	370					40
11/20/2000	640			13									220	390					34
11/30/2000	720			7									240	420					35
12/6/2000	760			10											0.1				33
12/13/2000				15									170						33
12/20/2000	1200	22		15									390						33
12/27/2000				24															33
1/3/2001	1300			29								1609	370						33
1/10/2001				26								1499							33.5
1/17/2001	900			25								1604	330						32
1/24/2001				28								1542							32
1/31/2001				21								1501							34
2/7/2001	1000			26								1482	340						32
2/14/2001				25								1504							34
2/21/2001	920			18								1503	330						32
2/28/2001				27								1478							32
3/7/2001	890			26								1409	310		39				34
3/14/2001				35								1330							35
3/21/2001	700			37								1143	230						36
3/28/2001				46								1032							34
4/4/2001	600	14		60								909	180		28				38
4/11/2001				110								649							40
4/18/2001	190	120		360								337	43						39
4/25/2001				360								344							46
5/2/2001	250	59		230								343	40		20				62
5/8/2001				220								345							62
5/14/2001	320	130		270								374	44						62
5/23/2001				65								568							62
5/30/2001				42								659							62
6/6/2001	570			30								698	120		30				64
6/13/2001				24								722	130						65
6/20/2001	750			18								807	150						65
6/27/2001				19								840	150						78
7/5/2001	810			16								940	180		42				65
7/11/2001				15								940	190						85
7/19/2001	830			13								958	200						80
7/24/2001				12								1022	210						77
8/1/2001	1100			8								1111	240		48				74
8/8/2001				15								1288	300						80

Table I.1-7 (continued)

Detected Analytes																			
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Total Silver (µg/L)	Dissolved Silver (µg/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)	Total Arsenic (µg/L)	Total Cadmium (µg/L)	Dissolved Cadmium (µg/L)	Conductivity (Field) (µS/cm)	Chloride (mg/L)	Hardness (mg/L)	Total Lithium (µg/L)	Low Level Mercury (ng/L)	Total Selenium (µg/L)	Dissolved Strontium (µg/L)	Temperature (°F)
8/14/2001	1200			21								1330	300						80
8/21/2001				9								1460	350						78
8/28/2001				12								1488	330						76
9/6/2001	1200			13								1486	370		62				80
9/10/2001				8								1450	360						66
9/18/2001	1200			12								1587	380						65
9/25/2001				9								1588	370						67
10/2/2001	1300			11								1639	370		85				64
10/10/2001				7								1250	370						55
10/15/2001	1300			5								1250	370						52
10/23/2001				6								1254	390						49
11/1/2001				11								1951	450						52
11/8/2001	1500			11								1910	420		76				46
11/14/2001				16								1912							52
11/18/2001	1600			17								1976	460						52
11/29/2001				17								1684							36
12/5/2001	770			27								1250	290		37				40
12/10/2001				22								1456							35
12/18/2001	750			24								1000	240						37
12/27/2001				25								1002							35
1/3/2002	900	63		33								1050	270		38				32
1/9/2002				38								1000							36
1/15/2002	970			42								1003	200						34
1/23/2002				48								820							34
1/29/2002				53								820							34
2/6/2002	570			48								800	180		33				35
2/12/2002				53								810							32
2/21/2002	630			58								800	190						35
2/25/2002				50								830							36
3/5/2002	560			59								770	170		33				32.5
3/13/2002												790							35
3/21/2002	570			61								880	170						34
3/26/2002				72								790							34
4/2/2002	540	26		73								840	160		45				39
4/10/2002				42								845							40
4/15/2002	320	58		160								447	64						55
4/23/2002				140								409							50
4/29/2002	340	45		270								375	59						43
5/8/2002				140								380							49
5/15/2002	290	29		230								400	62						51
5/21/2002	200			68								448	57						53
5/28/2002				66								375							68
6/4/2002	320	10		81								400	65						60
6/11/2002				63								411							65
6/17/2002	440			42								426	76						64
6/26/2002				32								504							72
7/3/2002	410			26								440	81		27				81
7/10/2002				27								420							77
7/17/2002	310			24								400	78						80
7/24/2002				21								395							74
7/30/2002				21								440							78
8/7/2002	290			21								395	85		40				71
8/14/2002				15								400							71.5
8/21/2002	380			19								440	99						68
8/28/2002				17								490							70
9/4/2002	420			19								495	110		31				69
9/11/2002				17								530							71
9/18/2002	490			12								633	130						66
9/25/2002		13	19	50								530							54
10/2/2002	370		28	43								500	100						59
10/9/2002		22	89	110								425							46
10/16/2002	350	40	46	160								450	85						44
10/23/2002		20	40	97								440							38
10/30/2002		18	59	91								460							39
11/6/2002	370	25	130	110								450	95		65				35
11/13/2002		15	32	83								460				1.7			36
11/20/2002	370	10	57	140								475	100						35
11/27/2002		6	39	60								500				0.7			35
12/4/2002	420	4.3	37	50								590	130		34				33
12/11/2002		4.3	31	26								620				1.1			33.5
12/18/2002	480		38	44								650	140			0.5			35
12/26/2002		3.3	35	44								640							33
1/2/2003	590	2.6	47	49								780	160		38				33
1/8/2003		1.9	34	45								840				0.8			34
1/15/2003	590	1.2	31	42								940	190						35
1/22/2003			30	40								980							34
1/30/2003		1.1	33	40								1000							34
2/5/2003	800	1.8	29	35								1100	250		48				34
2/12/2003		2.1	25	34								1100							34
2/19/2003	870	1.6	28	36								1100	280						33
2/28/2003		2.6	33	41								1100							33
3/5/2003	880	1.8	31	40								1100	290		50				33
3/12/2003		2		40								1200							34
3/19/2003	900	2.4	23	33								1200	300			2.5			35
3/26/2003		41	59	160								490							36
4/2/2003	210	34	52	250								250	40			2.2			36
4/9/2003		23	63	180								280							36
4/16/2003	250	45	44	200								330	52			2.4			37
4/23/2003		44	47	210								370							37
4/28/2003		34	46	180								440							47
5/7/2003	420	15	32	76								540	100		35	1.4			53
5/14/2003		15	31	82								390							52.5
5/21/2003	320	25	34	100								400	72						59
5/28/2003		7.5	29	50								440							64
6/5/2003	360	3.3	28	38								480	94		28	4.3			65
6/11/2003		4	22	35								470							61.5

Table I.1-7 (continued)

Detected Analytes																			
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Total Silver (µg/L)	Dissolved Silver (µg/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)	Total Arsenic (µg/L)	Total Cadmium (µg/L)	Dissolved Cadmium (µg/L)	Conductivity (Field) (µS/cm)	Chloride (mg/L)	Hardness (mg/L)	Total Lithium (µg/L)	Low Level Mercury (ng/L)	Total Selenium (µg/L)	Dissolved Strontium (µg/L)	Temperature (°F)
6/18/2003	410	4.3	17	32								430	82						72
6/25/2003		2.5	13	23								430							75.5
7/1/2003	360	2.5	16	20								435	93		30				70
7/9/2003		2	12	15								440							72
7/16/2003	360	1.9	9.2	15								480	100						70
7/22/2003		2	9.5	13								500							71
7/30/2003		1.7	10	12								520							75
8/6/2003	460	1.6	7.7	12									120		35	7.6			73
8/13/2003		3.2	5.6	10								540							73
8/20/2003	520	3	7.9	11								560	130						78
8/27/2003		2.3	5.5	7								540							73
9/4/2003	490	4.3	6.2	10								580	130		34				66
9/10/2003		3	7.8	9								590				3.9			70
9/17/2003	490	5	5.5	9								600	140						66
9/24/2003		4.6	5.6	10								610							58
10/1/2003		2.3	7	9								620							50
10/10/2003	490	2.3	7.3	10								750	170		38	0.7			57
10/15/2003	480	4.2	5.1	14								730	170						53
10/22/2003		5.7		11								760							49
10/29/2003		4.5		10								790							44
11/5/2003	700	4.3		9								820	210		42	5.2			39
11/12/2003		2	5.4	6								950							37
11/19/2003	760	4.3	5.1	12								1100	260						40
11/26/2003		4.1		9								1200							34
12/3/2003	940	1.6	6.7	8								1300	350		60	1			36
12/10/2003		2.7	9.2	9								1300							38
12/17/2003	1100	3.5	6.9	11								1500	420						37
12/23/2003		2.4	11	13								1600							35
12/30/2003		5.4	20	26								1100							34
1/7/2004	480	2.7	15	23								680	160		26	0.5			33
1/14/2004			16	23								680							33
1/21/2004	510		15	22								740	170						33
1/28/2004			15	22								840							33
2/4/2004	680	1.6	15	21								960	220		35	3.5			33
2/8/2004			16	22								980							33
2/15/2004	740	1.2	15	22								980	240						33
2/22/2004		1.5	15	20								1000							33
2/29/2004		1.7	16	21								1000							35
3/7/2004	690	1.3	19	24								920	220		30	0.5			34
3/14/2004		1.6	19	24								780							34
3/21/2004	710	1.3	17	22								840							34
3/28/2004		5.3	23	34								630							35
4/1/2004	290	42	55	210								330	66			4			34
4/10/2004		13	46	140								260							38
4/18/2004	240	14	44	130								280	46						48.5
4/25/2004		61	47	250								275							48.5
5/2/2004	240	52	42	250								315	48		26	3.2			52
5/9/2004		23	36	110								350							55
5/16/2004	330	20	33	98								400	65						56
5/23/2004		7.3	31	67								390							55
5/31/2004		12	39	99								390							58
6/6/2004	340	9	45	87								400	57		26	1.3			62
6/13/2004		5	35	53								420							68
6/20/2004	350	5	31	43								430	67						66
6/27/2004		5	29	42								490							64
7/5/2004	410	2.9	25	30								500	90		30	1.3			68
7/11/2004		3	22	29								510							68
7/18/2004	310	2.2	21	26								470	91						76
7/25/2004		2.5	18	23								440							69
8/1/2004	340	2.1	16	21								410	78		27				70
8/8/2004		1.7	17	19								390							67
8/15/2004	290	2.2	15	23								320	62						63
8/23/2004		5.3	16	33								350							67
8/30/2004		4.5	16	28								379							62.1
9/8/2004	320	2.5	18	28								446	67			1.1			61.9
9/13/2004		2.4	18	30								405							65.6
9/20/2004	270	6.7	16	41								400	53						61.8
9/27/2004		4.2	16	28								427							60.2
10/4/2004	220	2	17	32								439	55			0.6			48.3
10/11/2004		8.5	17	47								363							56.3
10/18/2004	290	16	20	70								398	49						43.5
10/25/2004		22	22	86								388							43.6
11/1/2004		15	21	71								377							49.8
11/7/2004	240	21	31	99								437	51			1.8			43.5
11/14/2004		22	32	110								427							41.6
11/21/2004	230	9	30	84								351	56						42
11/28/2004		18	34	99								449							42
12/6/2004	300	14	37	90								461	68			2.4			39
12/12/2004		5.5	41	84								560							34
12/19/2004	320	4	38	67								331	61						33
12/26/2004		3	37	62								215							24
1/2/2005	370	3.5	33	56								679	88		28	1.4			33
1/9/2005		1.5	45	54								651							34
1/16/2005	370	4	36	50								720	93						32
1/23/2005			40	53								754							32
1/30/2005		2	41	52								790							35
2/6/2005	510	6	36	48								420	120		38				38
2/13/2005		2.5	34	49								892							35
2/20/2005	460	3.5	44	54								752	94						33
2/27/2005		7	49	57								829							32
3/6/2005	510		43	57								755	120		41				36
3/13/2005			38	47								923							34
3/20/2005	610	8	41	53								867	160						36
3/27/2005			41	49								705							37
4/3/2005	280	31	50	150								387	55		26	2.3			38
4/10/2005		9	47	120								320							40

Table I.1-7 (continued)

Detected Analytes																			
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Total Silver (µg/L)	Dissolved Silver (µg/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)	Total Arsenic (µg/L)	Total Cadmium (µg/L)	Dissolved Cadmium (µg/L)	Conductivity (Field) (µS/cm)	Chloride (mg/L)	Hardness (mg/L)	Total Lithium (µg/L)	Low Level Mercury (ng/L)	Total Selenium (µg/L)	Dissolved Strontium (µg/L)	Temperature (°F)
4/17/2005	260	11	38	99								380	49						41
4/24/2005		3.5	28	53								409							40
5/1/2005	320	6	17	37								467	70			0.9			51
5/8/2005		3	22	39								515							64
5/15/2005	400		18	27								550	94						54
5/22/2005		3.5	16	26								355							60
5/30/2005		3	17	22								627							67
6/5/2005	420		13	20								609	98		27				71
6/12/2005			14	19								623							72
6/19/2005	380	4	11	17								425	90						77
6/26/2005		2.5	12	17								298							80
7/4/2005	350	3	9.6	17								578	100		32				71
7/10/2005			11	15								593							84
7/17/2005	370		8.1	14								585	100						87
7/24/2005		2.5	9.3	13								595							78
7/31/2005		2	7.2	11								589							72
8/7/2005	360		10	15								575	100		33				73
8/14/2005		2	9.2	15								596							70
8/21/2005	390		9.7	16								609	110						70
8/28/2005		5	6.7	17								625							70
9/5/2005	410	2	9.4	18								617	110		30				72
9/11/2005		5.5	16	28								662							72
9/18/2005	410	2	6.5	11								680	120						70
9/25/2005		5.2	6.2	12								691							66
10/2/2005	450	2.5	6.3	12								388	130		33				68
10/9/2005		5.5	11	35								694							54
10/16/2005	430	5	9.8	26								630	120						60
10/23/2005		6	11	27								686							54
10/30/2005		5	11	20								654							52
11/6/2005	560	3.5	8.1	17								802	160		31	0.7			49
11/13/2005		5.5	6.8	21								815							50
11/20/2005	600	4.5	14	26								386	150						38
11/27/2005		3	11	22								813							36
12/4/2005	460	2	15	25								830	130		29				36
12/11/2005		2	15	25								826							36
12/18/2005	550		20	32								873	140						34
12/25/2005		2.5	18	26								911							36
1/2/2006	560		19	28								752	150	270	32	0.7			32
1/8/2006		2.5	21	31								861		260					34
1/15/2006		2	25	36								822		250					36
1/22/2006			35	44								928		260					33
1/29/2006			35	42								920		300					34
2/5/2006	550	2	35	43								949	130	290					34
2/12/2006			33	42								1018		320					34
2/19/2006			37	43								1073		320					34
2/26/2006			33	41								1075		350					34
3/5/2006	680		37	42								1107	180	360					34
3/12/2006			31	39								1129		380					35
3/19/2006			31	40								1087		330					32
3/26/2006			35	45								999		290					34
4/2/2006	450	6	45	71								763	110	210		1.8			34
4/9/2006		7.5	40	110								415		130					37
4/16/2006		8.5	31	94								410		140					40
4/23/2006		5.5	31	77								311		150					41
4/30/2006		4.5	21	47								369		180					42
5/7/2006	380	3.5	15	30								343	100	200					43
5/14/2006		16	39	150								481		160					40
5/21/2006		8	26	63								537		170					43
5/29/2006		5	23	36								593		170					75
6/4/2006	400	4.5	20	29								629	98	190					75
6/11/2006		5	25	39								580		160					66
6/18/2006		3	24	30								604		180					76
6/25/2006		2	18	23								547		170					72
7/2/2006	430		16	19								648	110	180		0.8			75
7/9/2006		4.5	13	19								663		190					70
7/16/2006		18	10	23								554		190					85
7/23/2006		2	11	14								680		190					72
7/30/2006		2	10	11								623		180					74
8/6/2006	450	2.5	7.9	12								692	120	200					73
8/13/2006		3.5	5.2	8								696		200					71
8/20/2006		3.5	5.2	7								721		200					70
8/27/2006		7.5	5.6	10								746		210					71
9/4/2006	510	6	5.2	9								755	160	220					71
9/10/2006		9	5.2	10								757		110					66
9/17/2006		3.5	17	27								779		230					68
9/24/2006		5.5	8.4	15								793		230					60
10/1/2006	480	3	5.2	7								786	160	230		0.5			60
10/8/2006		3.5	8.2	12								835		240					54
10/15/2006		6	7.5	15								840		240					47
10/22/2006		8	6.3	9								888		260					38
10/28/2006		62	5.2	13								938		280					38
11/5/2006	650	3.5	5.2	6								1025	200	300					38
11/12/2006		5	5.2	6								1453		490					37
11/19/2006		2	5.2	7								1608		480					38
11/26/2006		2	8	12								1372		430					37
12/3/2006	780	5.5	8.1	15								1416	290	370					34
12/10/2006		2	5.2	19								1269		350					34
12/17/2006		2	14	19								1440		380					34
12/25/2006		2	15	20								1346		320					34
1/2/2007		2.5	14	19								1374		330					34
1/7/2007	900	4	17	24								1395	280	360		0.5			33
1/14/2007		2.5	22	28								1626	330	360					32
1/21/2007		2.5	24	29								1648		380					30
1/28/2007		2	23	25								1715		380					30
2/4/2007	980	2	23	28								1736	370	390					28
2/11/2007		2	21	25								1327		430					28

Table I.1-7 (continued)

Detected Analytes																			
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Total Silver (µg/L)	Dissolved Silver (µg/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)	Total Arsenic (µg/L)	Total Cadmium (µg/L)	Dissolved Cadmium (µg/L)	Conductivity (Field) (µS/cm)	Chloride (mg/L)	Hardness (mg/L)	Total Lithium (µg/L)	Low Level Mercury (ng/L)	Total Selenium (µg/L)	Dissolved Strontium (µg/L)	Temperature (°F)
2/18/2007		2	23	27								1688		440					32
2/25/2007		2	23	26								1739		460					32
3/4/2007	1200	2	22	26								1538	440	520					34
3/11/2007		2	23	25								1924		510					34
3/18/2007		2	30	42								1293		290					32
3/25/2007		3.5	46	97								637		170					35
4/1/2007	360	14	52	160								638	81	180		2.7			36
4/8/2007		16	53	220								657		180					34
4/15/2007		8	56	160								648		180					38
4/22/2007		12	52	130								665		190					48
4/29/2007		7	27	57								712		200					58
5/6/2007	480	6.5	23	42								769	110	220					56
5/13/2007		6.5	24	39								816		240					60
5/20/2007		3.5	18	28								720		260					54
5/28/2007		3.5	13	18								949		290					66
6/3/2007	580	2	14	18								1004	190	290					66
6/10/2007		3	19	19								880		290					72
6/17/2007		2	14	14								339		290					76
6/24/2007		2	12	13								983		270					76
7/1/2007	670	2	8.2	11								970	190	270		0.5			70
7/8/2007		2	8.6	15								912		270					80
7/15/2007		2.5	6	9								1029		280					72
7/22/2007		2	5.5	9								637		270					76.4
7/29/2007		2	5.2	5								830		280					74
8/5/2007	780	2	5.2	8								1001	230	280					70
8/12/2007		9	14	17								1064		300					75
8/19/2007		2.5	28	34								1719		480					65
9/30/2007	700	3	9.7	14								1112	240	290					16
10/7/2007	920	11	16	37								865	290	380		1.4			48
10/14/2007		12	23	65								865		240					48
10/21/2007		22	35	110								862		220					53
10/28/2007		12	34	80								866		240					46
11/4/2007	520	19	33	97								899	180	230					42
11/11/2007		15	37	88								924		250					39
11/18/2007		14	36	78								929		250					37
11/25/2007		12	34	66								1044		340					37
12/2/2007	630	5.5	35	56								1090	180	310					37
12/9/2007		7.5	37	50								1111		320					32
12/16/2007		2	33	48								1171		350					39
12/25/2007		4	37	45								1114		340					34
1/1/2008		3	40	51								1120		320					34
1/6/2008	670	2	42	50								1168	170	320		0.5			34
1/13/2008		2.5	45	54								1240		330					34
1/20/2008		2	50	58								1286		350					32
1/27/2008		5	52	64								1326		370					37
2/3/2008	730	2	56	65								1269	220	400					39
2/9/2008		5	53	62								1410		440					32
2/17/2008		2	52	61								1476		430					34
2/24/2008		2	49	58								1498		410					34
3/2/2008	870	2.5	49	55								1444	270	430					37
3/9/2008		4	45	50								1574		460					36
3/16/2008		2	51	56								1611		470					41
3/23/2008		3	33	45								1667		470					37
3/30/2008		3	39	47								1671		500					39
4/6/2008	830	7	23	41								1284	220	390		2			37
4/13/2008		7	50	74								800		210					35
4/20/2008		16	38	130								362		120					37
4/27/2008		52	48	230								453		150					39
5/5/2008	270	31	42	250								469	58	160					42
5/11/2008		24	38	170								490		150					47
5/18/2008		21	32	90								480		170					56
5/26/2008		16	26	62								270		200					59
6/1/2008	480	8.5	25	48								630	100	200					68
6/8/2008		3	23	31								660		230					67
6/15/2008		2	20	22								700		230					67
6/22/2008		2	13	18								710		240					70
6/29/2008		3.5	12	16								790		220					69
7/6/2008	550	2	10	13								840	13	240		0.5			72
7/13/2008		2	9.3	12								830		230					68.9
7/20/2008		2	9.3	11								770		210					77.3
7/27/2008		2	7.7	11								810		230					70
8/3/2008	570	2	7.2	9								860	150	230					75
8/10/2008		2	8.7	10								840		240					74.4
8/17/2008		2	10	10								870		240					74.3
8/24/2008		2	7.4	9								820		240					71
9/1/2008		3.5	12	14								850	170	250					80.5
9/7/2008	500	2	6.5	16								850		240					63
9/14/2008		2.5	10	12								850		250					61.6
9/21/2008		2	10	10								920		250					69
9/28/2008		2	7.2	11								850		250					55
10/5/2008	480	4.5	7.6	13								350	180	260		0.7			49
10/12/2008		2	11	13								980		270					57.3
10/19/2008		2	8.3	16								1030		330					52
10/26/2008		2	5.2	5								1000		290					46
11/2/2008	780	8.5	8.7	12								1040	230	340					42
11/9/2008		3.5	7.9	11								1020		320					43
11/16/2008		3.5	5.2	14								1110		360					39
11/23/2008		2	12	13								1220		370					34.6
11/30/2008		2	7.9	10								1250		360					38
12/7/2008	740	3	6.7	8								1310	280	420					34.5
12/14/2008		3	26	15								1530		480					39
12/21/2008		3	8.8	12								1530		520					37
12/28/2008		2	14	17								2020		610					37
1/4/2009	1100	2	17	18								1910	410	540		0.5			34
1/11/2009		2	16	18								1820		560					34
1/18/2009		2	14	17								1950		490					36

Table I.1-7 (continued)

Detected Analytes																			
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Total Silver (µg/L)	Dissolved Silver (µg/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)	Total Arsenic (µg/L)	Total Cadmium (µg/L)	Dissolved Cadmium (µg/L)	Conductivity (Field) (µS/cm)	Chloride (mg/L)	Hardness (mg/L)	Total Lithium (µg/L)	Low Level Mercury (ng/L)	Total Selenium (µg/L)	Dissolved Strontium (µg/L)	Temperature (°F)
1/25/2009		2	15	19								1920		500					33
2/1/2009	1200	2	14	19								1970	420	560					33
2/8/2009		2	15	19								1970		580					34
2/15/2009		4	24	27								1750		480					34
2/22/2009		2	16	17								1680		470					35
3/1/2009	1100	2	13	19								1940	430	500					35
3/8/2009		2.5	15	22								1940		450					35
3/15/2009		7	18	24								1950		470					38
3/22/2009		3.5	40	63								1130		260					38
3/29/2009		3	54	74								500		140					36
4/5/2009	260	3.5	41	75								420	64	140		1.4			38
4/12/2009		5.5	40	87								440		120					48
4/19/2009		10	22	56								400		130					49
4/26/2009		18	32	81								790		200					48
5/3/2009	460	16	28	110								750	140	210					51
5/10/2009		9.5	30	71								750		220					55
5/17/2009		7.5	25	52								790		220					54
5/25/2009		4	21	33								840		230					70
5/31/2009		2	19	24								960		240					51
6/7/2009	520	4	14	19								840	160	230					60.9
6/14/2009		4	11	14								830		240					70
6/21/2009		2	5.2	16								810		220					75
6/28/2009		2	11	14								840		230					72
7/5/2009	560	2	10	13								870	180	220					66
7/12/2009		2.5	13	13								830		230		0.7			71
7/19/2009		2	9.2	11								820		230					71
7/26/2009		2	9.5	12								820		220					70
8/2/2009	470	2	14	19								830	190	200		1.5			68
8/9/2009		2	11	11								830		210					71
8/16/2009		2	12	14								850		210					77
8/23/2009		2.5	9.1	10								900		240					65
8/30/2009		2.5	9.1	11								910		250					63
9/7/2009	690	2	8.1	11								970	230	270					68
9/13/2009		2	9.6	9								1000		280					71
9/20/2009		2	5.7	6								1030		280					67
9/27/2009		3	5.2	9								1060		320					64
10/4/2009	800	3	6.2	10								1040	250	320					52.8
10/11/2009		2	5.2	5								1420		500		0.5			45.6
10/18/2009		2	12	18								1260		340					40.4
10/25/2009		2.5	19	41								1110		270					41
11/1/2009	670	6.5	25	55								1000	200	220					44
11/8/2009		6.5	29	60								1040		250					41
11/15/2009		4	24	43								1070		270					42
11/22/2009		3.5	25	44								1100		310					40
11/29/2009		3	23	38								1130		290					38
12/6/2009	680	3	20	37								1140	230	310					33
12/13/2009		2	28	21								1160		300					33
12/20/2009		2	27	38								1180		310					33
12/27/2009		2	25	36								1190		310					33
1/3/2010	740	2	28	33								1230	240	310					33
1/10/2010		2	24	31								1250		330					32
1/12/2010																0.6			
1/17/2010		2	32	37								1240		330					33
1/24/2010		4.5	31	35								1270		350					33
1/31/2010		2	31	34								1260		340					32
2/7/2010	680	2	29	34								1240	230	330					33
2/14/2010		2	30	35								1270		330					33
2/21/2010		2	34	40								1300		380					33
2/28/2010		2.5	29	34								1310		400					34
3/7/2010	830	2	37	39								1350	260	420					34
3/14/2010		2	34	41								1220		350					35
3/21/2010		6.5	44	78								610		170					35
3/28/2010		5	46	80								590		170					37
4/4/2010	380	9	37	95								580	120	180					52
4/5/2010																1.1			
4/11/2010		16	26	58								640		190					47
4/18/2010		5	22	41								700		210					53
4/25/2010		5	18	32								740		240					53
5/2/2010	510	5	14	20								780	170	260					57
5/9/2010		2.5	9.8	21								830		280					55
5/16/2010		13	10	16								870		280					58
5/23/2010		2	13	15								880		290					67
5/30/2010		2	8.6	10								890		270					73
6/6/2010	660	2	8.3	10								880	210	280					65
6/13/2010		2.5	6.2	8								870		280					64
6/20/2010		2	9.2	11								890		270					72
6/27/2010		2	7.9	9								880		270					74
7/5/2010	760	2	5.2	9								920	220	270					78
7/11/2010		2	6.3	5								930		270					77
7/18/2010		2	5.2	8								990		320		0.5			75
7/25/2010		2	5.2	5								1030		300					75
8/1/2010	1400	48	5.2	5								1050	260	330					75
8/8/2010		6.5	9.8	9								1100		310					75
8/15/2010		2	5.2	5								1120		360					75
8/22/2010		2	5.2	6								560		380					67
8/29/2010		2	5.2	6								1200		400					71
9/6/2010	900	2	5.2	9								1240	400	380					64
9/12/2010		2	5.2	5								1250		400					61
9/19/2010		2	5.2	7								1250		410					56
9/26/2010		2	6.6	8								1540		480					56
10/3/2010	1200	2	5.2	5								1530		470					53
10/5/2010													340			0.5			
10/10/2010		3	6.9	22								1420		370					56
10/17/2010		3.5	8.2	11								1420		360					52
10/24/2010		2	5.4	8								1450		370					49
10/31/2010		2.5	8.2	11								1500		300					43

Table I.1-7 (continued)

Detected Analytes																			
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Total Silver (µg/L)	Dissolved Silver (µg/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)	Total Arsenic (µg/L)	Total Cadmium (µg/L)	Dissolved Cadmium (µg/L)	Conductivity (Field) (µS/cm)	Chloride (mg/L)	Hardness (mg/L)	Total Lithium (µg/L)	Low Level Mercury (ng/L)	Total Selenium (µg/L)	Dissolved Strontium (µg/L)	Temperature (°F)
11/7/2010	960	7.5	8.1	10			3.8					1440	310	380					41
11/14/2010		2	8.2	12								1420		420					43
11/21/2010		2	9.8	13								1580		390					33
11/28/2010		2	13	16								1600		410					34
12/5/2010	660	2	14	16			3.6					1620	340	400					33
12/12/2010		2	15	16								1180		410					33
12/19/2010		2	5.8	8								1720		430					33
12/28/2010		2	12	15								1760		460					34
1/3/2011	1100	2	18	22			5.5					1690	68	460					33
1/9/2011		2	24	27								1820		450					33
1/11/2011																0.5			
1/16/2011		2	23	26								1810		490					33
1/23/2011		2	21	28								1880		520					33
1/30/2011		2	23	23								1910		490					33
2/6/2011	1200	2	21	23			4.7					1950	390	530					33
2/13/2011		2	23	26								1980		570					34
2/20/2011		2.5	24	25								1840		540					33
2/27/2011		2	24	26								1980		530					33
3/6/2011	1300	2	21	23			5.5					2070	480	460					34
3/13/2011		2	19	22								2080		510					35
3/20/2011		2	29	40								1630		390					36
3/27/2011		2	44	67								780		220					36
4/3/2011	420	2	43	64			4.9					660	100	200					40
4/6/2011																1.5			
4/10/2011		2	41	68								480		220					46
4/17/2011		9	35	94								960		250					39
4/24/2011		10	40	81								950		280					45
5/1/2011	680	12	33	77			3.8					890	180	280					47
5/8/2011		10	34	75								960		270					52
5/15/2011		9.5	38	56								990		290					52
5/22/2011		5	13	28								1010		300					64
5/30/2011		5	30	43								950		280					60
6/5/2011	630	8	45	91			6.4					860	160	240					65
6/12/2011		5.5	36	48								870		250					63
6/19/2011		2	30	32								810		250					67
6/26/2011		2	22	28								920		260					66
7/5/2011	650	2	15	18			5.8					960	180	260					78
7/10/2011		2	15	18								960		270					76
7/17/2011		2	15	17								960		270					78
7/19/2011																0.5			
7/24/2011		2	16	13								930		260					73
7/31/2011		2.5	11	13								910		230					76
8/7/2011	660	2	7.9	9			5.5					910	210	210					77
8/14/2011		2	8.6	10								920		240					72
8/21/2011		2	7.6	6								920		220					72
8/28/2011		2	8.2	13								960		250					71
9/4/2011	700	2	20	21			5.5					990	210	240					69
9/11/2011		2	7	14								980		240					72
9/18/2011		3	7.5	11								1010		250					58
9/25/2011		3	5.2	8								1000		270					57
10/3/2011	690	2.5	5.2	5			5.8					990	220	270					53
10/4/2011																0.6			
10/9/2011		2.5	5.2	8								1000		270					63
10/16/2011		2	5.2	7								1020		240					52
10/23/2011		5.5	5.2	11								1050		290					47
10/30/2011		3.5	5.4	10								1100		300					44
11/6/2011	870	2.5	7.1	9			5.6					1220	300	380					44
11/13/2011		2	7.3	10								1520		530					40
11/20/2011		3.5	7.4	12								1610		500					35
11/27/2011		4	12	19								1460		420					37
12/4/2011	910	2	14	22			4.5					1470	350	370					35
12/11/2011		3	15	22								1550		370					34
12/18/2011		2	17	23								1590		390					34
12/26/2011		3.5	27	34								1640		410					34
1/2/2012	1100	4	15	21			5.8					1690	410	440					33
1/4/2012																0.6			
1/9/2012		2	15	19								1720		440					35
1/15/2012		3	16	20								1770		470					33
1/23/2012		2.5	16	21								1810		460					34
1/29/2012		2	15	25								1870		480					33
2/5/2012	1200	2	18	21			5.4					1880	510	470					33
2/12/2012		2	19	24								1930		530					33
2/19/2012		2	18	21								1990		530					33
2/26/2012		2	18	22								2020		530					33
3/4/2012	1500	2	17	18			5.6					2030	480	500					33
3/11/2012		2.5	37	33								1870		510					34
3/18/2012		19	57	130								550		160					40
3/25/2012		3.5	33	69								810		200					51
4/1/2012	480	18	40	110			5					800	180	210					45
4/8/2012		6	27	58								830		220					49
4/10/2012																0.6			
4/15/2012		4	27	63								890		240					53
4/22/2012		4.5	26	45								900		250					50
4/29/2012		4.5	24	33								940		280					52
5/6/2012	700	3	23	31			4.9					980	10	290					57
5/13/2012		2	19	32								980		240					60
5/20/2012		2	19	24								1040		290					68
5/28/2012		4	18	22								1070		300					65
6/3/2012	920	2.5	20	23			5.6					1090	240	290					64
6/10/2012		2	20	21								1130		270					75
6/17/2012		2	17	20								1130		280					69
6/24/2012		2	12	17								1170		320					71
7/1/2012	860	2	14	16			4.9					1170	270	290					77
7/8/2012	920	2	11	24								1170	270	300					79
7/10/2012																0.6			
7/15/2012		2	10	13								1190		290					81

Table I.1-7 (continued)

Detected Analytes																			
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Total Silver (µg/L)	Dissolved Silver (µg/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)	Total Arsenic (µg/L)	Total Cadmium (µg/L)	Dissolved Cadmium (µg/L)	Conductivity (Field) (µS/cm)	Chloride (mg/L)	Hardness (mg/L)	Total Lithium (µg/L)	Low Level Mercury (ng/L)	Total Selenium (µg/L)	Dissolved Strontium (µg/L)	Temperature (°F)
7/22/2012		2	11	11								1200		290					78
7/29/2012		2	11	13								1200		290					76
8/5/2012	840	2	5.4	10			4.9					1190	300	280					73
8/12/2012		2	5.4	23								1200		270					70
8/19/2012		3.5	5.2	5								1320		300					69
8/27/2012		2	5.2	8								1430		370					73
9/3/2012	1100	2	6.1	8			5.4					1530	370	370					75
9/9/2012		2	5.2	5								1420		370					67
9/16/2012		2	5.5	5								1450		390					63
9/23/2012		2	5.2	7								1460		380					54
9/30/2012		2	5.5	7								1500		340					54
10/7/2012	1300	2	10	13			5.8					1520	400	380					47
10/14/2012		3	5.3	9								1630		380					47
10/21/2012		2	8.5	21								1510		390					49
10/25/2012																1			
10/28/2012		6.5	34	56								1250		340					42
11/4/2012	940	2.5	20	31			4.9					1330	310	310					37
11/11/2012		3	19	31								1310		340					42
11/18/2012		2.5	24	45								1280		330					37
11/25/2012		2	27	30								1350		280					34
12/2/2012	850	2	14	17			4.4					1350	300	330					34
12/9/2012		2	26	40								1340		350					33
12/16/2012		2	25	31								1350		360					35
12/23/2012		2	27	32								1420		360					33
12/30/2012		2	28	33								1470		390					34
1/6/2013	900	2	26	32			4.8					1540	360	440					33
1/10/2013																0.5			
1/13/2013		2.5	29	37								1560		150					34
1/20/2013		2	5.2	12								1620		380					34
1/27/2013		2	28	34								1670		390					33
2/3/2013	1200	2	28	36			5.2					1750	390	390					33
2/10/2013		2	33	40								1730		400					33
2/17/2013		2	28	40								1720		360					33
2/24/2013		2	26	42								1740		500					34
3/3/2013	1100	2	28	31			5.9					1730	400	470					34
3/10/2013		2	21	26								1740		440					33
3/17/2013		2	26	39								1710		460					33
3/24/2013		2	25	30								1750		460					32
3/31/2013		2	34	31								1690		460					34
4/7/2013	910	2	25	34			5.9					1450	320	380		1.1			35
4/14/2013		2	33	39								1530		410					35
4/21/2013		3	49	74								910		260					34
4/28/2013		4	43	74								590		190					39
5/5/2013	310	5.5	83	120			6.6					460	82	210					39
5/12/2013		10	71	130								460	90	180					47
5/19/2013		10	64	100								480		150					58
5/27/2013		14	36	90								500		140					58
6/2/2013	390	8.5	51	77			6.8					540	96	190					63
6/9/2013		9.5	36	55								580		190					63
6/10/2013		7	30	51										190					
6/16/2013	340	3	33	40								620	96	210					68
6/23/2013		6	30	36								650		210					65
6/30/2013		3.5	29	31								650		180					70
7/7/2013	510	2	13	24			4.8					680	120	190					75
7/10/2013																0.5			
7/14/2013		2	21	28								690		200					72
7/21/2013		2	21	25								720		220					76
7/28/2013		2	19	24								770		230					65
8/4/2013	630	2	18	20			8.5					810	160	240					70
8/11/2013		2.5	7.4	14								810		220					69
8/18/2013		2	21	19								830		260					70
8/25/2013		2	17	13								860		240					75
9/2/2013	710	2	15	18			5.9					870	170	390					71
9/8/2013		2.5	5.2	18								870		240					65
9/15/2013		2.5	11	16								870		250					65
9/22/2013		2	13	27								880		230					59
9/29/2013		2.5	5.2	16								890		260					60
10/6/2013	660	2	9.3	13			6.4					910	180	260					58
10/13/2013		2	5.3	5								910		260					57
10/20/2013		2	5.2	17								890		290					49
10/21/2013																0.5			
10/27/2013		3	18	22								1100		320					41
11/3/2013	740	2	15	23			7.9					1080	250	300					40
11/10/2013		3	15	53								1100		350					38
11/17/2013		3.5	28	40								1120		360					37
11/25/2013		5.5	17	87								1110		310					33
12/1/2013	690	2	31	28			4.2					1140	230	330					34
12/8/2013		2	39	43								1200		350					33
12/15/2013		2	53	61								1230		340					33
12/22/2013		2	34	47								1260		330					33
12/29/2013		2	30	44								1310		350					33
1/7/2014	920	2	5.2	39			5.5					1340		380					33
1/12/2014		2	5.2	27								1350	290	410					33
1/13/2014																1.1			
1/19/2014		2	7.5	34								1400		450					33
1/26/2014		2	34	51								780		460					33
2/2/2014	910	3	29	15			5.3					1460	350	440		0.5			33
2/9/2014		2	21	44								1500		410					33
2/16/2014		2	23	32								1550		560					33
2/23/2014		2	33	44								1570		460					33
3/2/2014	960	2	48	49			5.7					1590	400	470					33
3/9/2014		2	36	36								1610		480					33
3/16/2014		3	30	35								1600		480					33
3/23/2014		2	17	35								1580		460					33
3/30/2014		2	24	38								1570		460					33
4/6/2014	980	2	30	38			5.5					1460	320	350					33

Table I.1-7 (continued)

Detected Analytes																			
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Total Silver (µg/L)	Dissolved Silver (µg/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)	Total Arsenic (µg/L)	Total Cadmium (µg/L)	Dissolved Cadmium (µg/L)	Conductivity (Field) (µS/cm)	Chloride (mg/L)	Hardness (mg/L)	Total Lithium (µg/L)	Low Level Mercury (ng/L)	Total Selenium (µg/L)	Dissolved Strontium (µg/L)	Temperature (°F)
4/8/2014																0.5			
4/13/2014		2	38	64								920		250					33
4/18/2014			33	88			6.2												
4/20/2014		3	45	67								990		150					35
4/27/2014		4	37	81								320		100					37
5/4/2014	300	18	39	110			4.6					410	79	130					40
5/11/2014		20	43	210								430	80	130					53
5/18/2014		12	36	160								470		140					53
5/25/2014		2	42	75								520		140					68
6/1/2014	440	4	36	49			5					570	95	160					70
6/8/2014		4	33	53								540		150					65
6/15/2014		4	25	44								560		210					60
6/22/2014		2.5	23	27								610		180					68
6/29/2014		4.5	19	24								640		190					74
7/6/2014	240	2	13	17			4.7					640	120	190					74
7/13/2014		2	12	16								680		170					71
7/14/2014																1.1			
7/20/2014		2	9.2	13								710		200					72
7/27/2014		2	9	12								690		210					74
8/3/2014	580	2	6.7	15			5.1					720	140	210					74
8/10/2014		2	7.3	11								1020		230					80
8/17/2014		2.5	5.2	9								N/A		240					N/A
8/24/2014		2.5	6.8	10								810		230					71
9/1/2014		3	14	23								780		200					68
9/7/2014	640	2	20	31			5.5					840	190	210					65
9/14/2014		7.5	73	52								980	170	220					54
9/21/2014		3	72	45								980		230					57
9/28/2014		5.5	29	39								1030		250					64
10/5/2014	540	6	21	33			5.7					1040	180	240					52
10/7/2014																0.8			
10/12/2014		3	21	32								1070	310	250					49
10/19/2014		5	22	37								1090		210					47
10/20/2014	580				<12		5.4	45	0.72	<0.10			190	250	20	0.38	<1.4		
10/21/2014	590				<12		5.3	45	0.73	<0.10			190	240	14	0.29	<1.4		
10/21/2014	600				<12		5.4	45	0.65	<0.10			190	250	18	0.27	<1.4		
10/26/2014		2.5	27	35								1100		250					48
11/2/2014	600	2.5	21	36			5.3					1130	190	240					41
11/9/2014		5	24	38								1200		290					38
11/17/2014		2.5	31	41								1210		310					34
11/23/2014		2	32	41								1230		300					34
11/30/2014		2	38	43								1240		290					34
12/7/2014	760	2	36	38			5.5					1320	140	260					34
12/14/2014		2	39	38								1310		320					36
12/21/2014		2	36	41								1040		240					35
12/28/2014		2	32	46								840		210					35
1/4/2015	440	2	36	43			5.3					930	130	230					33
1/12/2015		2	41	42								1000		270					33
1/13/2015																1.2			
1/18/2015		2	38	39								850		270					35
1/25/2015		2	30	34								880		270					34
2/1/2015	640	2	36	38			4.8					1130	190	310					34
2/8/2015		3	41	43								1210		310					33
2/16/2015		2	40	44								1290		340					33
2/22/2015		2	39	47								1340		350					33
2/26/2015	650				15		5.5	57	<1.0	<0.10			230	390	70	0.3	2.6		
2/26/2015	680				16		5.5	59	<1.0	<0.10			240	400	68	0.5	2.3		
3/1/2015	590	2	36	41			5.1					1390	210	380					33
3/5/2015	680				15		5.6	58	<1.0	<0.10			240	390	60	0.48	2.3		
3/8/2015		2	34	40								1450		370					34
3/15/2015		4.5	34	54								1200		280					34
3/16/2015	550	4	32	53			5.1						190	250					
3/22/2015		7	36	88								600		140					34
3/29/2015		5	33	65								570		150					37
4/6/2015	310	11	35	89			4.2					610	84	140					39
4/12/2015		3.5	30	45								740		180					45
4/17/2015																1.1			
4/19/2015		5	23	47								850		210					53
4/26/2015		6.5	22	50								880		250					46
4/28/2015	510				<0.30		4.4	40	<2.0	<0.10			170	210	34	6	1.1		
4/29/2015	570				<0.30		4.2	42	<2.0	<0.10			170	200	34	0.99	1.2		
5/3/2015	580	2.5	25	34			4					930	150	250					58
5/10/2015		4.5	21	24								1000		210					56
5/17/2015		2.5	18	24								1040		260					60
5/25/2015		2	14	15								1070		240					64
5/31/2015		5	13	18								1100		260					61
6/7/2015	730	2	13	17			4.4					1110	180	250					65
6/14/2015		2	14	14								1130		240					68
6/21/2015		2	9.8	15								1170		260					66
6/28/2015		2	9.6	12								1180		260					73
7/5/2015	810	2.5	8.7	10			3.4					1240	240	260		0.6			71
7/12/2015		2	8.9	10								1220		250					76
7/19/2015		2	8.5	9								1250		270					75
7/26/2015		2.5	8.2	10								1290		310					76
8/2/2015	920	2	7	7			4.9					1310	220	280					74
8/9/2015		2	5.6	7								1470		270					71
8/12/2015					<10				<10	<1				300	62		<10		
8/12/2015					<10				<10	<1				300	56		<10		
8/16/2015		2.5	5.9	6								1390		300					77
8/23/2015		2	5.2	5								1370		270					68
8/30/2015		2	5.2	7								1390		280					68
9/7/2015	930	2	5.2	7			4.2					1380	330	320					76
9/13/2015		4	5.2	6								1560		390					65
9/20/2015		2	7.3	8								1570		350					66
9/27/2015		2	5.3	9								1580		330					64
10/4/2015	960	2	5.2	6			4.2					1600	340	330					55
10/6/2015																0.5			

Table I.1-7 (continued)

Detected Analytes																			
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Total Silver (µg/L)	Dissolved Silver (µg/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)	Total Arsenic (µg/L)	Total Cadmium (µg/L)	Dissolved Cadmium (µg/L)	Conductivity (Field) (µS/cm)	Chloride (mg/L)	Hardness (mg/L)	Total Lithium (µg/L)	Low Level Mercury (ng/L)	Total Selenium (µg/L)	Dissolved Strontium (µg/L)	Temperature (°F)
10/11/2015		2	5.2	5								1600		320					55
10/18/2015		2	5.2	7								1700		330					47
10/20/2015	860				<10		5.3	54	<10	<3			330	350	72	0.31	2.5		
10/21/2015	850				<10		6.4	51	<10	<3			340	350	63	1.5	2.5		
10/25/2015		3	5.2	5								1620		320					47
11/1/2015	850	2	5.2	6			4.3					1610	380	320					46
11/8/2015		3.5	9.9	15								1620		360					45
11/15/2015		11	26	70								1400		280					39
11/22/2015		12	28	72								1370		280					35
11/29/2015		6	34	67								1420		270					34
12/6/2015	850	2	30	49			4.8					1370	260	290					35
12/13/2015		2	31	46								1240		240					36
12/20/2015		6.6	38	76								1070		230					32
12/27/2015		8	36	60								1020		230					33
1/3/2016	460	3	35	55			4.6					940	150	210					33
1/10/2016		2	34	45								930	150	220		0.7			33
1/17/2016		2	36	45								920	140	250					33
1/24/2016		2	33	41								950	170	220					33
1/31/2016		2		42								970							33
2/8/2016	480	2	36	38			4.6					980	150	260					33
2/14/2016		2	32	42								1000	150	270					33
2/21/2016		2	36	41								990		250					33
2/28/2016		2	34	41								1020		250					34
3/6/2016	620	2	35	37			4.9					1110	160	280					33
3/13/2016		2	31	36								930		190					35
3/16/2016			35	49			4												
3/20/2016		2	29	54								460		140					35
3/28/2016		2	28	62								430		100					38
4/4/2016	250	3	28	65			3					490	62	110		0.8			35
4/10/2016		2	25	43								640	96	140					36
4/17/2016		2.5	23	41								700		170					51
4/24/2016		2	21	37								790		200					49
5/1/2016	440	3.5	22	50			3.9					770	120	170					50
5/8/2016		4.5	20	38								830	130	200					60
5/15/2016		3	18	32								900		230					54
5/22/2016		2	21	23								950		260					66
5/30/2016		5.5	15	21								970		240					65
6/5/2016	560	2	15	20			4.2					920	160	250					64
6/12/2016		2.5	15	23								890	160	210					70
6/19/2016		2	13	18								890		190					74
6/26/2016		2	12	14								880		190					75
7/4/2016	620	2	9.9	3			2.7					890	160	200		0.5			74
7/10/2016		2	8.6	11								910	190	220					74
7/17/2016		2	16	22								910		200					73
7/24/2016		2	15	17								920	200	210					80
7/31/2016		2	12	13								960		200					76
8/2/2016	620	4	12	11	0.5		4.5		1	0.2			190	170			1		
8/8/2016				10								970					1		76
8/14/2016				6								960					1		73
8/22/2016				27								990					1		70
8/25/2016				7			5												
8/28/2016				5								1070					2.5		72
9/5/2016	780	4	4.5	6	0.5		4.9		1	0.2		1100	220	350			1		71
9/11/2016				19								1000					1		67
9/18/2016				18								1040					1		66
9/25/2016				12													1		
10/2/2016	640	4.5	15	20	0.5		5.1		1	0.2		1050	200	180		0.5	1		59
10/6/2016				21			4.5												
10/10/2016				25								1100					1		54
10/16/2016				16								1110					1		51
10/23/2016				19								1100					1		49
10/30/2016				22								1120					1		46
11/6/2016	660	4	12	24	0.5		5		1	0.2		1150	220	250			1		48
11/13/2016				30								1210					1		44
11/20/2016				22								1300					1		38
11/28/2016				32								1240					1		37
12/4/2016	590	8	20	42	0.5		4.3		1	0.2		1180	250	250			1		36
12/11/2016				37								1240					1		33
12/19/2016				27								1290					1		33
12/26/2016				24								1330					1		33
1/2/2017	680	5.3	23	33	0.5		4.4		1	0.2		1370	270	230			1		33
1/5/2017																0.5			
1/8/2017				27								1410					1		33
1/15/2017				36								1470					1.2		33
1/19/2017				33			4.5												
1/23/2017				45								1480					1.8		33
1/29/2017				47								1460					1.2		34
2/5/2017	790	4	33	37	0.5		5		1	0.2		1560	300	370			1		33
2/12/2017				31								1570					1.4		33
2/19/2017				34								1570					1		33
2/26/2017				42								860					1		33
3/1/2017				49			3.6												
3/5/2017	330	4	27	44	0.5		3.7		1	0.2		730	120	180			1		33
3/13/2017				42								690					1		34
3/20/2017				39								650					1		37
3/27/2017				42								650					1		39
4/3/2017	350	4	21	25	0.5		3.2		1	0.2		670	110	140		0.7	1		45
4/9/2017												880							49
4/10/2017				26													1		
4/12/2017				26			3.1												
4/17/2017				21								870					1		51
4/24/2017				27								870					1		48
5/1/2017	440	5	45	74	0.5		3.5		1	0.2		790	130	180			1		43
5/8/2017				44								790					1		52
5/15/2017				34								840					1		59
5/22/2017				56								720					1		51

Table I.1-7 (continued)

Detected Analytes																			
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Total Silver (µg/L)	Dissolved Silver (µg/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)	Total Arsenic (µg/L)	Total Cadmium (µg/L)	Dissolved Cadmium (µg/L)	Conductivity (Field) (µS/cm)	Chloride (mg/L)	Hardness (mg/L)	Total Lithium (µg/L)	Low Level Mercury (ng/L)	Total Selenium (µg/L)	Dissolved Strontium (µg/L)	Temperature (°F)
5/29/2017				41								740					1		62
6/4/2017	430	4	30	54	0.5		4.4		1	0.2		770	130	170			1		64
6/11/2017				33								780					1		71
6/18/2017				26								790					1		72
6/25/2017				21								800					1		69
7/2/2017	480	4	13	15	0.5		3.8		1	0.2		820	150	170		0.5	1		68
7/9/2017				15								800					1		74
7/12/2017				17			4.2												
7/16/2017				9.3								800					1		72
7/23/2017				11								810					1		74
7/24/2017	520				0.5				1	0.2						0.5	1		
7/30/2017				11								830					1		78
8/6/2017	480	4	7.9	7.6	0.5		4.2		1	0.2		840	170	150			1		71
8/13/2017				6.4								870					1		71
8/21/2017				13								910					1		70
8/27/2017				15								930					1		65
9/4/2017	630	4	10	14	0.5		4.2		1	0.2		960	190	200			1		66
9/10/2017				8.6								1040					1		61
9/17/2017				14								1010					1		68
9/24/2017				17								1070					1		71
10/1/2017	700	4	9.8	12	0.5		4.3		1	0.2		1100	230	240		0.2	1		61
10/4/2017				11			4.3												
10/8/2017				15								1100					1		58
10/15/2017				18								1130					1		53
10/22/2017				18								1140					1		55
10/29/2017				42								1080					3.3		41
11/5/2017	510	4	28	47	0.5		4.6		1	0.2		970	180	200			1		36
11/12/2017				41								990					1		34
11/19/2017				42								1010					1		34
11/26/2017				38								980					1		34
12/3/2017	450	4	23	34	0.5		4.4		4.5	0.2		920	160	230			3.2		36
12/10/2017				39								910					2.9		33
12/17/2017				36								880					2.9		33
12/25/2017				37								910					1.2		33
1/1/2018	480	4	25	33	0.5		4.5		2.2	0.2		990	180	240			1		32
1/7/2018				31								1030					1		32
1/11/2018				34			4.5												
1/14/2018				31								1100					1		33
1/21/2018				32								1120					1		32
1/28/2018				30								1130					1		33
2/4/2018	580	4	26	29	0.5		4.2		2.8	0.2		1170	200	280			1		32
2/11/2018				31								1210					1		33
2/18/2018				32								1230					1		33
2/25/2018				28								1290					1		32
3/5/2018	720	4	25	28	0.5		4.4		1	0.2		1320	250	310			1		33
3/12/2018				30								1360					4.1		33
3/19/2018				22								1390					2.8		34
3/26/2018				24								690					4.3		34
4/2/2018	720	4	25	32	0.5		4.8		1	0.2		690	290	390			2.3		34
4/4/2018				32													0.6		
4/6/2018				32													0.3		
4/8/2018				31								1440					3.5		34
4/11/2018				30			4.9												
4/16/2018				18								1440					1.8		34
4/22/2018				16								1370					1.8		37
4/25/2018				41			4.8												
4/30/2018				41								620					1		40
5/7/2018	310	4	24	37	0.5		3.4		3.6	0.2		530	88	140			1		56
5/13/2018				35								660					1		55
5/21/2018				13								770					1		60
5/28/2018				19								850					1		73
6/3/2018	560	4	13	7	0.5		4		1	0.2		880	170	230			1		66
6/10/2018			10	5								900					1		70
6/17/2018				11								870					1		74
6/24/2018			9.9	11								870					1		72
7/1/2018	520	5	9.5	2.5	0.5		3.4		1	0.2		800	160	46			1		75
7/8/2018			9.5	13								800					1		74
7/15/2018			10	3.4								880					1		78
7/18/2018				10			3.7												
7/22/2018			8.5	4.6								890					1		73
7/29/2018			6.7	8.3								890					1		72
8/5/2018	670	4	5.3	5.6	0.5		4.1		1	0.2		870	210	130			1		71
8/12/2018			5.4	5.1								820					1		77
8/19/2018			2.5	3.8								950					1		74
8/26/2018			2.5	4								960					1		71
9/3/2018	720	10	11	11	0.5		7		1	0.2		930	260	230			3.2		70
9/9/2018			11	9.6								980					1		65
9/16/2018			10	6.5								950					1		70
9/23/2018			7.3	6.4								990					1.9		60
9/30/2018			7.6	11								1040					1		53
10/7/2018	670	13	11	32	0.5		4.4		1	0.2		930	270	220			1		41
10/14/2018				60								660					1.6		40
10/17/2018				49			4.5												
10/21/2018			22	65								690					1.4		41
10/28/2018				47								700					1		44
11/4/2018	470	4	19	31	0.5		4.4		1	0.2		750	160	200			1		41
11/11/2018			23	47								720					1		33
11/18/2018				40								760					1		33
11/25/2018				39								790					1		34
12/2/2018	470	4	32	44	0.5		4.3		1	0.2			160	220			1		34
12/9/2018				35								740					1		33
12/16/2018			31	37								780					1		34
12/24/2018				30								820					1		33
12/31/2018				29								840					3.1		33
1/6/2019	570	4	30	32	0.5		4.7		1	0.2		840	180	280		0.5	1		33
1/10/2019				32			4.7												

Table I.1-7 (continued)

Detected Analytes																			
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Total Silver (µg/L)	Dissolved Silver (µg/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)	Total Arsenic (µg/L)	Total Cadmium (µg/L)	Dissolved Cadmium (µg/L)	Conductivity (Field) (µS/cm)	Chloride (mg/L)	Hardness (mg/L)	Total Lithium (µg/L)	Low Level Mercury (ng/L)	Total Selenium (µg/L)	Dissolved Strontium (µg/L)	Temperature (°F)
1/13/2019			28	28								850					1		33
1/20/2019				25								880					2.7		33
1/28/2019			28	28								920					1		33
2/3/2019	700	4	27	27	0.5		4.5		1	0.2		950	220	300			1		33
2/10/2019			24	29								990					1		33
2/18/2019			23	22								930					1		33
2/24/2019			21	23								920					1		33
3/4/2019	650	4	21	26	0.5		4.4		1	0.2		1060	250	350			1		33
3/11/2019			21	24								1100					1		33
3/18/2019			21	35								940					2.3		33
3/25/2019			26	33								790					1		33
3/31/2019			25	34								480					1.2		34
4/3/2019				43			3.7												
4/8/2019	220	8	25	34	0.5		3.3		1	0.2		330	60	120		0.8	1		40
4/15/2019			22	39								300					1		36
4/22/2019			21	37								300					1		40
4/29/2019			23	35								390					1		47
5/6/2019	340	10	23	36	0.5		3.1		1	0.2		430	220	140			1		53
5/13/2019			25	41								440					1.1		53
5/20/2019			20	32								470					1.1		51
5/27/2019			22	38								470					1		61
6/2/2019	410	4	18	25	0.5		3.7		1	0.2		510	110	190			1		63
6/9/2019			16	19								550					1		70
6/16/2019				16								550					1		67
6/23/2019			11	13								580					1		71
6/30/2019			9.7	13								610					1.5		75
7/7/2019	540	4	8.6	9.5	0.5		3.8		1	0.2		640	140	220		0.7	1		78
7/10/2019				9			3.7												
7/14/2019			7.1	7.9								680					1.1		75
7/21/2019			6.1	7.2								640					1		76
7/28/2019			5.5	6.1								640					1.8		77
8/4/2019	540	4	4.8	5.2	0.5		4.1		1	0.2		720	150	190		*G	1.2		77
8/11/2019			5	5.4													1		
8/12/2019												760							76
8/18/2019			4.3	9.4								790					2.9		73
8/25/2019			4.1	5.9								760					1		70
9/2/2019	580	4	4.1	4.6	0.5		4.6		1	0.2		780	160	210		*G	1		65
9/8/2019			3.4	4.3								770					1.5		63
9/15/2019			3.5	4.4								760					1		64
9/22/2019			3.9	5								790					1		70
9/29/2019			3.2	4.8								730					1		61
10/6/2019	690	5	4.4	7	0.5		4.3		1	0.2		910	190	300		0.5	1		55
10/9/2019				15			4.3												
10/13/2019			7.7	14								880					1		50
10/20/2019			10	14								880					3.6		47
10/27/2019			14	23								940					2.8		43
11/3/2019	610	10	15	23	0.5		4.2		1	0.2		1040	240	240			2.4		36
11/10/2019			18	26								1120					1		34
11/17/2019			21	22								1150					1		33
11/24/2019			22	24								1150					1		35
12/1/2019	740	10	27	32	0.5		5		1	0.2		1140	260	92			1		35
12/8/2019			26	29								1140					1		34
12/16/2019			29	29								1100					1		33
12/22/2019			30	31													1		
12/29/2019			27	30								1060					1		34
1/5/2020	650	4	26	30	0.5		4.7		1	0.2		1000	230	260		0.5	1		33
1/8/2020							4.9												
1/12/2020			26	29								910					1		33
1/20/2020			25	33								890					3.3		33
1/26/2020			25	27								940					1.7		33
2/2/2020	430	4	25	25	0.5		4.4		1	0.2		1020	190	240			2.7		33
2/9/2020			28	28								1030					3		33
2/16/2020			26	29								1050					2.5		33
2/23/2020			26	26								1100					1		33
3/2/2020	690	4	24	27	0.5		4.4		1	0.2		1160	230	330			1		33
3/9/2020			23	25								1180					1		33
3/16/2020				27								1100					1		33
3/23/2020				34								880					1		33
3/30/2020												570							35
4/1/2020							4.1												
4/6/2020	200	4	29		0.5		3.6		1	0.2		300	38	110		0.9			38
4/13/2020			23									380							36
4/20/2020			23	60								400					1		39
4/22/2020				48			3.3												
4/27/2020			18	44													1		
5/4/2020	310	4	21	35	0.5		4.1		1	0.2		520	91	160			1		53
5/11/2020			13	26								550					1		49
5/18/2020			14	21								590					1		54
5/25/2020			13	15								670					1		69
6/1/2020	380	4	14	19	0.5		3.6		1	0.2		590	110	170			1		64
6/7/2020			13	16								650					1		67
6/14/2020			13	18								720					1		64
6/21/2020			13	16								800					1		71
6/28/2020			12	13								800					1		75
7/5/2020	600	4	9.9	11	0.5		3.9		1	0.2		850	170	190		0.5	1		83
7/8/2020				10			3.7												
7/12/2020			9.7	11								840					1		78
7/19/2020			7.6	8.6								830					1		78
7/26/2020			6.5	8.7								860					1		78
8/2/2020	590	4	5.5	6.4	0.5		4		1	0.2		870	180	190			1		75
8/9/2020			4.9	5.4								790					1		77
8/16/2020			4.8	7.1								830					1		75
8/23/2020			5.1	6.2								850					1		75
8/30/2020			3.9	5.2								850					1		70
9/7/2020	550	4	3.9	4	0.5		5.1		1	0.2		860	200	220			1		64
9/13/2020			3.5	4.5								860					1		61

Table I.1-7 (continued)

Detected Analytes																			
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Total Silver (µg/L)	Dissolved Silver (µg/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)	Total Arsenic (µg/L)	Total Cadmium (µg/L)	Dissolved Cadmium (µg/L)	Conductivity (Field) (µS/cm)	Chloride (mg/L)	Hardness (mg/L)	Total Lithium (µg/L)	Low Level Mercury (ng/L)	Total Selenium (µg/L)	Dissolved Strontium (µg/L)	Temperature (°F)
9/20/2020			3.7	4.8								880					1		59
9/27/2020			3.2	4.5								870					1		63
10/4/2020	560	10	4.1	5	0.5		4.4		1	0.2		960	230	240		0.5	1		54
10/7/2020			4.7	5.5															
10/11/2020			4.5	6.4								1040					1		53
10/18/2020			6	8.9								1030					1		45
10/25/2020			11	18								1100					1		36
11/1/2020	770	4	15	24	0.5		4.4		1	0.2		1120	270	230			1		34
11/8/2020			18	33								1140					1		45
11/16/2020			14	24								1170					1		37
11/22/2020			20	36								1170					1		34
11/29/2020			19	33								1200					1		34
12/6/2020	790	10	19	26	0.5		5.6		1	0.2		1250	300	320			1		34
12/13/2020			18	24								1270					1		35
12/20/2020			17	23								1320					1		34
12/27/2020			18	27								1360					1		33
1/3/2021	900	<4.0	19				4.2						320	360		<0.50			
1/6/2021							4.5												
1/10/2021			19																
1/17/2021			17																
1/24/2021			29																
1/31/2021			19																
2/8/2021	850	<4.0	18				4.9						390	380					
2/14/2021			21																
2/21/2021			20																
2/28/2021			18																
3/8/2021	940	<4.0	18				5.2						390	410					
3/14/2021			26										270						
3/18/2021							5.1												
3/22/2021			24										110						
3/25/2021							4.4												
3/29/2021			23										120						
4/4/2021																0.99			
4/4/2021			26											170					
4/4/2021	440	25					3.6						110						
4/12/2021			21										120						
4/18/2021			17																
4/21/2021							3.5												
4/23/2021		4																	
4/26/2021		4	15																
5/3/2021	490	<10	16				3.7						150	200					
5/10/2021			15																
5/17/2021			13																
5/24/2021			12																
5/24/2021		<10						32					180			<0.50			66
5/31/2021			11																
6/7/2021	660	<10	9.6				3.9						200	230					
6/14/2021			7.9																
6/20/2021			7.1																
6/27/2021			6																
7/5/2021	620	7.9	5.5				4						200	220					
7/5/2021																<0.50			
7/9/2021							4.3												
7/11/2021			4.8																
7/18/2021			4.7																
7/25/2021			4.3																
8/1/2021	690	<4.0	3.8				4.4						200	210					
8/8/2021			3.5																
8/15/2021			3.2																
8/22/2021			3.2																
8/29/2021			3																
9/6/2021	730	8	2.5				4.7						210	230					
9/12/2021			2.5																
9/19/2021			3.3																
9/26/2021			2.6																
10/3/2021																<0.50			
10/4/2021	720	9	2.9				4.3						210	230					
10/10/2021			3.2																
10/17/2021			2.5																
10/24/2021			2.8																
10/31/2021			3.7																
11/7/2021	550	<4.0	3.9				4.2						230	250					
11/14/2021			3.8																
11/21/2021			4.5																
11/28/2021			8.6																
12/5/2021	840	4	11				3.7						350	380					
12/9/2021							4												
12/19/2021			18																
12/26/2021			17																
1/2/2022	710	<4.0	18				4.1						310	300					
1/2/2022																<0.50			
1/9/2022			20																
1/12/2022							4.8												
1/16/2022			28																
1/23/2022			24																
1/30/2022			23																
2/6/2022	720	<4.0	25				5						350	370					
2/13/2022			20																
2/20/2022			18																
2/27/2022			17																
3/7/2022	950	<4.0	16				5.2						820	470					
3/14/2022			18										780						
3/21/2022			17																
3/27/2022			27																
3/30/2022							4.8												
4/3/2022	340	<4.0	33				4.7						86	170		1.0			

Table I.1-7 (continued)

Detected Analytes																			
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Total Silver (µg/L)	Dissolved Silver (µg/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)	Total Arsenic (µg/L)	Total Cadmium (µg/L)	Dissolved Cadmium (µg/L)	Conductivity (Field) (µS/cm)	Chloride (mg/L)	Hardness (mg/L)	Total Lithium (µg/L)	Low Level Mercury (ng/L)	Total Selenium (µg/L)	Dissolved Strontium (µg/L)	Temperature (°F)
4/7/2022							4.4												
4/11/2022			35																
4/18/2022			34																
4/25/2022			31																
5/2/2022	260	14	26				2.3						68	120					
5/9/2022			22																
5/16/2022			19																
5/23/2022			16																
5/30/2022			18																
6/6/2022	380	<4.0	19				4.3						85	190					
6/13/2022			15																
6/20/2022			17	23													<1		
6/27/2022			15	17													<1		
7/3/2022	350	<4	12	14	<0.5		4.3		<1	<0.2			87	170		0.86	<1		
7/8/2022							4.2												
7/11/2022			17	19													<1		
7/18/2022			14	17													<1		
7/25/2022			12	15													<1		
7/31/2022				13													<1		
8/7/2022	430	<4	14	9.9	<0.5		4.9		<1	<0.2			100	170			<1		
8/14/2022			11	13													<1		
8/21/2022			7.8	11													<1		
8/28/2022			6.9	10													<1		
9/5/2022	360	<4	5.4	7.3	<0.5		4.2		<1	<0.2			100	170			<1		
9/12/2022			5.6	6.2													<1		
9/19/2022			4.7	5.3													<1		
9/25/2022				5.2															
9/25/2022			4.8	4.5													<1		
10/2/2022	370	<4	5.3	5.8	<0.5		4.3		<1	<0.2			110	180		<0.5	<1		
10/5/2022				5.2			4.6												
10/9/2022			5	5.1													<1		
10/16/2022			3.7	5.8													<1		
10/23/2022			9.8	18													<1		
10/30/2022				14															
10/30/2022			9.3	11													<1		
11/6/2022	430	7	8.2	50	<0.5		3.9		<1	<0.2			140	200			<1		
11/13/2022			23	48													<1		
11/20/2022			21	37													<1		
11/27/2022			24	35													<1		
12/4/2022	380	<4	21	34	<0.5		4.4		<1	<0.2			120	160			<1		
12/11/2022			27	32													<1		
12/18/2022			26	36													<1		
12/26/2022			26	33													<1		
1/2/2023	400	<4	34		<0.5		5		<1	<0.2			130	220		<0.5	<1		
1/8/2023			30	29													<1		
1/11/2023				28			4.9												
1/15/2023			30	35													<1		
1/22/2023			32	34													<1		
1/29/2023			31	33													<1		
2/5/2023	320	<4	27	29	<0.5		4.7		<1	<0.2			<10	230			<1		
2/12/2023			24	27													<1		
2/19/2023			22	28													<1		
2/26/2023			37	27													<1		
3/1/2023				32															
3/3/2023				32															
3/6/2023	490	<4	25	32	<0.5		5.3		<1	<0.2			150	270			<1		
3/8/2023				31															
3/10/2023				31															
3/13/2023			28	32													<1		
3/15/2023				29															
3/17/2023				29															
3/20/2023			24	29													<1		
3/22/2023				33															
3/24/2023				32															
3/27/2023			26	31													<1		
3/29/2023				31															
3/31/2023				33															
4/3/2023	400	<4	23	32	<0.5		4.7		<1	<0.2			120	260		<0.5	<1		
4/5/2023				29															
4/7/2023				31															
4/9/2023			26	31													<1		
4/10/2023				32															
4/12/2023				45			3.5												
4/14/2023				40															
4/17/2023			19	31													<1		
4/19/2023				68															
4/21/2023				50															
4/24/2023			19	40													<1		
4/26/2023				46															
4/28/2023				41															
5/1/2023	250	7.1	15	49	<0.5		2.9		<1	<0.2			61	130			<1		
5/3/2023				68															
5/5/2023				50															
5/8/2023			19	40													<1		
5/10/2023				37															
5/12/2023				32															
5/15/2023			22	33													<1		
5/17/2023				31															
5/19/2023				36															
5/22/2023			50	32													<1		
5/24/2023				28															
5/26/2023				26															
5/29/2023			15	25													<1		
5/31/2023				21															
6/5/2023	330	4.9	13	18	<0.5		3.4		<1	<0.2			86	180			<1		
6/8/2023	310	<4					3.4	<15					87	170		1.5			

Table I.1-7 (continued)

Detected Analytes																			
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Total Silver (µg/L)	Dissolved Silver (µg/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)	Total Arsenic (µg/L)	Total Cadmium (µg/L)	Dissolved Cadmium (µg/L)	Conductivity (Field) (µS/cm)	Chloride (mg/L)	Hardness (mg/L)	Total Lithium (µg/L)	Low Level Mercury (ng/L)	Total Selenium (µg/L)	Dissolved Strontium (µg/L)	Temperature (°F)
6/11/2023			11	16													<1		
6/18/2023			9.4	12													<1		
6/25/2023			8	10													<1		
7/4/2023	280	<4	7.6	15	<0.5		3.5		<1	<0.2			98	160		0.68	<1		
7/9/2023			7.1	7.5													<1		
7/13/2023				7.3			3.6												
7/16/2023			6	6.5													<1		
7/23/2023			5.7	7.4													<1		
7/30/2023			5	6.2													<1		
8/6/2023	420	<4	5.1	6.3	<0.5		3.6		<1	<0.2			110	150			<1		
8/13/2023			5.9	7.2													<1		
8/20/2023			6.6	7.5													<1		
8/27/2023			4.7	6															
9/4/2023	420	<4	5	5.7	<0.5		4.2		<1	<0.2			120	180			<1		
9/10/2023			7.1	6													<1		
9/17/2023			3.5	5													<2		
9/24/2023			4	5													<1		
10/1/2023	430	<4	2.9	4	<0.5		5		<1	<0.2			120	200		<0.5	<1		
10/8/2023			3	4.1													<1		
10/11/2023				4.3			4												
10/15/2023			3.2	4.1													<1		
10/22/2023			5	4.5													<1		
10/29/2023			3	3.5													<1		
11/5/2023	420	<4	3.3	4.5	<0.5		4.2		<1	0.23			130	210			<1		
11/12/2023			4.2	5													<1		
11/19/2023			4.2	5.5													<1		
11/26/2023			5.3	5.3													<1		
12/3/2023	550	<4	4.7	5.4	<0.5		4.5		<1	<0.2			180	330			<1		
12/10/2023				5.3													<1		
12/17/2023	850	<10	9.9	11			4.4	37					270	430		<0.5	<1		
12/25/2023			9.7	13													<1		
12/31/2023			12	14													<1		
1/7/2024	570	<4	13	15	<0.5		3.6		<1	<0.2			190	240		<0.5	<1		
1/14/2024			11	17													<1		
1/21/2024			11	17													<1		
1/25/2024				15			3.4												
1/28/2024			14	14													<1		
2/4/2024	550	<4	11	16	<0.5		3.6		<1	<0.2			230	310			<1		
2/11/2024			18	22													<1		
2/18/2024			16	24													<1		
2/25/2024			19	24													<1		
3/1/2024				23															
3/4/2024	630	<4	20	15	<0.5		4		<1	<0.2			210	250			<1		
3/6/2024				20															
3/8/2024				19															
3/11/2024			22	21													<1		
3/13/2024				21															
3/15/2024				20															
3/18/2024			15	18													<1		
3/20/2024				16															
3/22/2024				16															
3/25/2024			14	16													<1		
3/27/2024				29															
3/29/2024				25															
3/31/2024			17	22													<1		
4/1/2024				25															
4/3/2024				25			3.6												
4/5/2024				31															
4/8/2024	690	4	24	37	<0.5		3.5		<1	<0.2			220	220		0.52	<1		
4/10/2024				33															
4/12/2024				26															
4/15/2024			17	25													<1		
4/17/2024				21															
4/19/2024				20															
4/22/2024			18	22													<1		
4/24/2024				24															
4/26/2024				24															
4/29/2024			17	24													<1		
5/1/2024				23															
5/3/2024				23															
5/6/2024				25															
5/6/2024	760	5	17	25	<0.5		3.6		<1	<0.2			290	300			<1		
5/8/2024				25															
5/10/2024				23															
5/13/2024			15	24													<1		
5/15/2024				20															
5/17/2024				18															
5/20/2024			14	14													<1		
5/22/2024				16															
5/24/2024				16															
5/27/2024			13	16													<1		
5/29/2024				14															
5/31/2024				13															
6/2/2024	900	<4	11	24	<0.5		4.2		<1	<0.2			270	270			<1		
6/9/2024			9.4	13													<1.0		
6/16/2024			9.2	11													<1.0		
6/23/2024			11	13													<1.0		
6/30/2024			15	18													<1.0		

Notes:

Prepared by: KRM2, LDC

Checked by: DCF1

1. Nitrate as N detected on 5/24/2021 (0.1 mg/L) and 12/17/2023 (0.1 mg/L) was excluded due to lack of consistent data.

2. Cyanide detected on 5/24/2021 (0.006 mg/L) and 12/17/2023 (0.005 mg/L) was excluded due to lack of consistent data.

3. Phosphorus detected in 1999, 2000, 2023, and 2024 (1.78 mg/L total detected over 44 sampling events) was excluded from table due to lack of consistent data.

4. Blank cells represent an analyte not tested during sampling event.

5. Significant figures are as reported from the database obtained from White Pine Copper.

mg/L = milligram per liter

µg/L = microgram per liter

Appendix Table I.1-7a
Surface Water Quality - Perch Creek Outfall (001A)
White Pine Copper LLC

Detected Analytes															
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Total Silver (µg/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)	Total Arsenic (µg/L)	Total Cadmium (µg/L)	Dissolved Cadmium (µg/L)	Chloride (mg/L)	Hardness (mg/L)	Low Level Mercury (ng/L)	Total Selenium (µg/L)	Total Strontium (µg/L)
7/7/2024	560	5	17	18	<0.50	4.4		<1.0	<0.20		180	190	<0.50	1	<1.0
7/10/2024				18		4.5								1	
7/14/2024			13	15										1	<1.0
7/21/2024	650	<10	9.5	10		4.5	28					220	<0.50	1	<1.0
7/28/2024			8.6	9.8										1	<1.0
8/3/2024	660	<4.0	7.6	8.3	<0.50	4.8		<1.0	<0.20		220	230		1	<1.0
8/11/2024			5.7	7.3										1	<1.0
8/18/2024			7.8	5.6										1	<1.0
8/25/2024			5.6	6.8										1	<1.0
10/8/2024			3.3	6.1										1	<1.0
10/15/2024			240	290										1	<1.0
10/22/2024			11	19											<1.0
10/28/2024	690	4.1	7.1	11	<0.50	5.4		1.1	<0.20		230	260		1	<1.0
11/4/2024	710	<4.1	21	26	<0.50	5.6		<1.0	<0.20		240	330	1.3		<1.0
11/12/2024			14	24											<1.0
11/18/2024			22	27										1	<1.0
11/20/2024				26		4.6									
11/25/2024			16	24										1	<1.0
12/1/2024	500	<4.0	18	27	<0.50	4.4		<1.0	<0.20		190	230		1	<1.0
12/9/2024			16	27										1	<1.0
12/15/2024			22	33										1	<1.0
12/22/2024			31	30											<1.0
12/29/2024			27	33											<1.0
1/5/2025	350	<4.0	22	26	<0.50	5.2		<1.0	<0.20		110	200	0.94	1	<1.0
1/8/2025				27		5.8								1	
1/12/2025			30	31										1	<1.0
1/19/2025			38	34										1	<1.0
1/26/2025			32	33											<1.0
2/2/2025	350	<4.0	25	28	<0.50	5.3		<1.0	<0.20		100	230		1	<1.0
2/9/2025			23	31											<1.0
2/16/2025			23	32										1	<1.0
2/23/2025			28	29											<1.0
3/3/2025	480	<4.0	25	27	<0.50	5.5		<1.0	<0.20		140	270			<1.0
3/10/2025			24	26										1	<1.0
3/16/2025			26	35											<1.0
3/19/2025				43		4.5								1	
3/21/2025				48											
3/24/2025			26	44											<1.0
3/26/2025				39											
3/28/2025				44											
3/31/2025			25	41											<1.0
4/2/2025				35										<1.0	
4/4/2025				35											
4/7/2025	180	<4.0	<25	31	<0.50	3.6		<1.0	<0.20		35	120	0.77	<1.0	<1.0
4/13/2025			25	42											<1.0
4/17/2025						<7.0									
4/18/2025				69										<1.0	
4/21/2025			22	61											<1.0
4/23/2025				53											
4/25/2025				57										<1.0	
4/28/2025			20	54											<1.0
4/30/2025				50											
5/2/2025				46										<1.0	
5/5/2025	280	<4.0	19	37	<0.50	3.7		<1.0	<0.20		68	130			<1.0
5/7/2025				40											
5/9/2025				36										<1.0	
5/12/2025			19	33											<1.0
5/14/2025				28											
5/16/2025				26										<1.0	
5/19/2025			17	21										<1.0	<1.0
5/21/2025				20											
5/23/2025				19										<1.0	
5/26/2025			13	16										1.6	<1.0
6/2/2025	360	6	8.9	13	<0.50	4.1		<1.0	<0.20		100	210		<1.0	<1.0
6/8/2025			8.3	12											<1.0
6/15/2025			7.3	9.5										<1.0	<1.0
6/22/2025			6.7	8.8											1.6
6/29/2025			6.3	9.1										<1.0	<1.0
7/9/2025				7.2		4.6									
7/13/2025			5.7	6.6										<1.0	<1.0
7/20/2025			7	8.1										<1.0	<1.0
7/27/2025				11											
8/3/2025	430	<4.0	7.1	10	<0.50	4.8		<1.0	<0.20		140	200		<1.0	<1.0
8/10/2025			11	7.1										<1.0	<1.0
8/17/2025			4.2	5.9										1.7	<1.0
8/24/2025			3.9	6.6										<1.0	<1.0

Table I.1-7a (continued)

Detected Analytes															
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Total Silver (µg/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)	Total Arsenic (µg/L)	Total Cadmium (µg/L)	Dissolved Cadmium (µg/L)	Chloride (mg/L)	Hardness (mg/L)	Low Level Mercury (ng/L)	Total Selenium (µg/L)	Total Strontium (µg/L)
9/1/2025	470	<4.0	3.7	4.4	<0.50	4.6		<1.0	<0.20		150	220		2.5	<1.0
9/7/2025			3.7	6										<1.0	1.7
9/14/2025			3.6	4.3											<1.0
9/21/2025			3.1	4.3										<0.50	2.5
9/28/2025			3.3	4.6										<1.0	<1.0
10/5/2025				5.4									<0.50	<1.0	
10/5/2025	600	4.1	3.7		<0.050	7.2		1	<0.20		190	290	<0.50	<1.0	<0.50
10/12/2025			5.3	6.7										<1.0	<1.0
10/19/2025			5.9	4.9										<1.0	<1.0
10/26/2025			3.6	4.3										<1.0	<1.0
11/2/2025	650	<4.0	3.9	5.3	<0.50	4.8		1.1	<0.20		220	290			<1.0
11/9/2025			6	5.4										<1.0	<1.0
11/16/2025	720	<4.0	5.7	5.2	<0.50	4.7		<1.0	<0.20		260	320		<1.0	<1.0
11/19/2025				5.7		4.4								<1.0	
11/23/2025			5.8	5.9											<1.0
11/30/2025			7.3	11										<1.0	<1.0
12/7/2025	690	<4.0	16	20	<0.50	4.1		1.3	<0.20		260	260	<0.50	<1.0	<1.0
12/14/2025			17	17										<1.0	<1.0
12/21/2025			14	14											<1.0
12/28/2025			13	15											<1.0
1/4/2026	730	<4.0	20	24	<0.50	5.2		1.1	<0.20		260	310	<0.50	<1.0	<1.0
1/7/2026				35		5.9								<1.0	
1/11/2026			26	35									<0.50	<1.0	<1.0
1/18/2026			34	34											<1.0
1/25/2026			28	40										<1.0	<1.0
2/1/2026	640	<4.0	33	36	<0.50	6.3		1.2	<0.20		230	320		<1.0	<1.0
2/8/2026			22	27											<1.0
2/15/2026			24	29											<1.0
2/22/2026			23	29										<1.0	<1.0
3/1/2026	730	<4.2	26	26	<0.50	6.4		1.2	<0.20		260	340			<1.0
3/9/2026			26	34											<1.0
3/11/2026				30											
3/13/2026				26										<1.0	
3/16/2026			25	27											<1.0
3/18/2026				29										<1.0	
3/20/2026				32											
3/23/2026			28	32											<1.0
3/25/2026				31		5									
3/27/2026				35										<1.0	
3/30/2026			30	33							66				<1.0
4/1/2026				36											
4/3/2026				37											
4/5/2026	250	<4.0	25	41	<0.50	4.6		<1.0	<0.20	<0.20	53	160	0.6	<1.0	<1.0
4/6/2026				39											
4/8/2026				37		4.5									
4/10/2026				33											
4/13/2026			23	31							43			<1.0	<1.0
4/15/2026				34											
4/17/2026				35											
4/20/2026			20	110										<1.0	
4/22/2026				73											
4/24/2026				64											
4/27/2026			21	52										<1.0	
4/29/2026				70											
5/1/2026				100											
5/4/2026	230	7.2	18	66	<0.50	3.6		<1.0		<0.20	61	130		<1.0	
5/6/2026				64											
5/8/2026				66											
5/12/2026			17	49										<1.0	
5/13/2026				43											
5/15/2026				31											
5/18/2026			18	25										<1.0	
5/20/2026				23											
5/22/2026				23											
5/25/2026			12	19										<1.0	
5/27/2026				21											
5/29/2026				25											
6/1/2026	330	<4.0	11	15	<0.50	4.2		<1.0		<0.20	81	170		<1.0	
6/7/2026			11	13										<1.0	
6/14/2026			1.7	12										<1.0	
6/21/2026			9.1	11										<1.0	

Notes:

Prepared by: KRM2, LDC

1. Blank cells represent an analyte not tested during sampling event.

Checked by: DCF1

2. Significant figures are as reported from the database obtained from White Pine Copper.

mg/L = milligram per liter

µg/L = microgram per liter

Appendix Table I.1-8
Surface Water Quality - Portal Creek
White Pine Copper LLC

Detected Analytes												
Date	Lab	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Hardness (mg/L)	Chloride (mg/L)	Calcium Dissolved (mg/L)	Dissolved Organic Carbon (mg/L)	Dissolved Magnesium (µg/L)	pH (Lab) (SU)	Sulfate (mg/L)
6/26/2011	Lab - General		<4	34	38	140					7.57	
6/10/2013	Lab - General		4	60	64	94						
5/4/2014	Lab - General	65	6	120	130	45	<10				7.64	
7/6/2014	Lab - General	20	<8	24	36	110	<10				7.98	
8/3/2014	Lab - General	230	16	6.3	65	180	<10				7.11	
9/7/2014	Lab - General	130	<4	37	40	99	<10				7.46	
10/5/2014	Lab - General	110	19	36	44	95	<14				7.68	
11/2/2014	Lab - General	120	<4	36	38	99	<10				7.96	
4/6/2015	Lab - General	73	5	66	74	48	<10				7.46	
5/3/2015	Lab - General	120	<4	38	46	110	<10				7.62	
6/7/2015	Lab - General	110	<4	32	35	93	<10				7.68	
7/5/2015	Lab - General	150	<8	22	25	120	<10				7.29	
9/7/2015	Lab - General			71		110		33				
10/4/2015	Lab - General	170	<4	9.5	12	130	<10				7.38	
11/1/2015	Lab - General	100	<4	24	28	100	<10				7.81	
12/6/2015	Lab - General	120	<4	36	37	97	<10				7.81	
4/3/2016	Lab - General	68	<4	56	65	52	<10				7.55	
5/1/2016	Lab - General	89	<4	47	55	75	<10				7.76	
6/5/2016	Lab - General	170	<4	51	60	140	<10				7.97	
7/4/2016	Lab - General	140	<4	11	20	120	<10				7.34	
8/7/2016	Lab - General	170	<4	7.6	9.9	150	<10				7.29	
9/5/2016	Lab - General	150	8	10	17	140	<10				7.41	
10/2/2016	Lab - General	100	<4	23	27	110	<10				7.77	
11/6/2016	Lab - General	150	<4	13	19	130	<10				7.76	
12/4/2016	Lab - General	99	<4	22	27	96	<10				7.64	
1/2/2017	Lab - General	120	<4	14	19	120	<10				7.6	
2/5/2017	Lab - General	120	<4	24	27	100	<10				7.48	
3/5/2017	Lab - General	77	<4	34	41	89	<10				7.57	
4/3/2017	Lab - General	60	<4	42	60	54	<10				7.64	
5/1/2017	Lab - General	120	13	79	130	75	<10				7.82	
6/4/2017	Lab - General	110	<4	34	43	93	<10				7.57	
7/2/2017	Lab - General	140	<4	18	20	110	<10				7.54	
8/6/2017	Lab - General	150	<4	9.4	11	140	<10				7.54	
9/4/2017	Lab - General	160	<4	17	21	110	<10				7.68	
10/1/2017	Lab - General	140	<4	8	9.2	130	<10				7.33	
11/5/2017	Lab - General	94	4	44	49	80	<10				7.71	
12/3/2017	Lab - General	110	<4	35	42	82	<10				7.63	
3/5/2018	Lab - General	140	21	21	44	130	<10				7.45	
4/2/2018	Lab - General	96	7	26	34	120	<10				7.45	
5/7/2018	Lab - General	100	7	57	70	77	<10				7.41	
6/3/2018	Lab - General	150	<4	24	29	130	<10				7.71	
7/1/2018	Lab - General	120	46	38	70	89	<10				7.76	
8/5/2018	Lab - General	140	6	20	26	120	<10	37			7.33	
10/7/2018	Lab - General	130	8	21	36	97	<10				7.79	
11/4/2018	Lab - General	120	<4	31	39	95	<10	28			7.54	
12/2/2018	Lab - General	100	<4	34	39	90	<10				7.76	
1/6/2019	Lab - General	140	<4	30	31	110	<10				7.67	
2/3/2019	Lab - General	140	<4	26	28	120	<10	35			7.16	
4/8/2019	Lab - General	49	45	75	110	52	<10				7.15	
5/6/2019	Lab - General	100	7	10	62		<10				7.59	
6/2/2019	Lab - General	130	5	34	39	93	<10	27			7.49	
7/7/2019	Lab - General	170	<4	12	13	130	<10				7.61	
8/4/2019	Lab - General	190	7	4.3	6.5	150	<10				7.25	
10/6/2019	Lab - General	140	8	21	30	110	<10				7.76	
11/3/2019	Lab - General	120	<4	31	45	95	<10				7.83	
12/1/2019	Lab - General	120	7	38	31	280	<10				7.61	
2/4/2020	Lab - General	10	<4	32	37	94	<10				7.4	
3/2/2020	Lab - General	260	<4	26	34	110	<10				7.66	
4/6/2020	Lab - General	120	<4	64	66	51	<10				7.47	
5/4/2020	Lab - General	82	<4	49	47	65	<10				7.75	
6/1/2020	Lab - General	88	<4	42	46	92	<10				7.47	
7/5/2020	Lab - General	190	8	6.4	8.7	160	<10				7.13	
8/2/2020	Lab - General	220	10	4.6	6.7	180	<10				7.15	
10/4/2020	Lab - General	40	<4	12	14	120	<10				7.36	
11/1/2020	Lab - General	130	<4	20	24	99	<10				7.52	
12/6/2020	Lab - General	150	<4	23	26	120	<10				7.76	
1/3/2021	Lab - General	130	<4	22	26	110	<10				7.72	
3/8/2021	Lab - General	130	<4	17	67	120	<10				7.42	
4/4/2021	Lab - General	120	<4	54	67	66	<10				7.59	
5/3/2021	Lab - General	10	5	42	52	83	<10				7.73	
6/7/2021	Lab - General	150	8	27	28	110	<10				7.71	
7/5/2021	Lab - General	160	4	21	25	130	<10				7.55	
9/6/2021	Lab - General	250	6	8.5	11	220	<10					
10/3/2021	Lab - General	210	19	25	32	160	<10				7.63	

Table I.1-8 (continued)

Detected Analytes												
Date	Lab	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Hardness (mg/L)	Chloride (mg/L)	Calcium Dissolved (mg/L)	Dissolved Organic Carbon (mg/L)	Dissolved Magnesium (µg/L)	pH (Lab) (SU)	Sulfate (mg/L)
11/7/2021	Lab - General	180	6	22	31	140	<10				7.6	
12/5/2021	Lab - General	180	<4	28	31	110	<10				7.6	
4/3/2022	Lab - General	130	7	49	60	86	<10				6.96	
5/2/2022	Lab - General	100	8	84	110	50	<10				7.02	
6/6/2022	Lab - General	130	<4	40	45	110	<10				7.77	
7/3/2022	Trace	160	<4	24	25	140	<10				7.64	
8/7/2022	Trace	180	<4	22	24	140	<10				7.56	
9/5/2022	Trace	280	<4			190	<10				7.5	
10/2/2022	Trace	180	<4	14	13	150	<10				7.41	
11/6/2022	Trace	120	6	28	37	110	<10				7.77	
12/4/2022	Trace	130	<5.3	36	50	93	<10				7.26	
1/2/2023	Trace	110	<4	38	40	100	<10				7.05	
4/3/2023	Trace	80	<4	32	37	120	<10				7.67	
4/19/2023	Trace	80	18	76	89							
5/1/2023	Trace	86	32	70	110	57	<10				7.78	
6/5/2023	Trace	180	28	33	67	140	<10				7.57	
7/4/2023	Trace	160	<4	28	27	130	<10				7.77	
7/17/2023	Trace	120	6	22	91							
9/12/2023	Trace	300	<4	13	15							
10/1/2023	Trace	260	<4	11	13	200	<10				6.73	
10/17/2023	Trace	240	<4	11	10							
11/5/2023	Trace	200	<4	22	25	160	<10				7.5	
11/20/2023	Trace	89	<4	24	31							
12/3/2023	Trace	170	<4	30	43	140	<10				7.61	
12/20/2023	Trace	130	<4	39	42							
1/7/2024	Trace	140	<4	44	46	110	<10				7.55	
2/4/2024	Trace	<40	<4	33	52	130	<10				7.5	
3/4/2024	Trace	160	<4	42	48	97	<10				7.69	
3/23/2024	Trace	120	<4	39	47							
4/8/2024	Trace	120	17	60	65	62	<10				7.76	
4/18/2024	Trace	<40	<4	77	88							
5/6/2024	Trace	98	<4	70	70	85	<10				7.66	
5/19/2024	Trace	130	<4	52	62							
5/29/2024	Trace			36	47	140	<10	40	10	8	7.64	<15
6/2/2024	Trace	160	<4	34	38	130	<10				7.75	
6/12/2024	Trace			31	35	140	<10	42	11	8.3	7.73	<3
6/20/2024	Trace	160	<4	60	59							

Notes

Prepared by: KRM2, LDC

Checked by: DCF1

1. Sample of Arsenic, Total Recoverable (1.0 ug/L) taken on 12/1/2019 was excluded from the table due to limited data.
2. Sample of Cadmium, Total Recoverable (0.2 ug/L) taken on 12/1/2019 was excluded from table due to limited data.
3. Selenium, Total Recoverable (1.0 ug/L) taken on 12/1/2019 was excluded from the table due to limited data.
4. Silver, Total Recoverable (0.5 ug/L) taken on 12/1/2019 was excluded from the table due to limited data.
5. Total Organic Carbon (6.5 mg/L) taken on 2/4/2020 was excluded from the table due to limited data.
6. Blank cells represent an analyte not tested during that event.
7. Significant figures are as reported from the database obtained from White Pine Copper.

mg/L = milligram per liter

µg/L = microgram per liter

Appendix Table I.1-8a
Surface Water Quality - Portal Creek
White Pine Copper LLC

Detected Analytes											
Date	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Hardness (mg/L)	Chloride (mg/L)	Calcium Dissolved (mg/L)	Dissolved Organic Carbon (mg/L)	Dissolved Magnesium (µg/L)	pH (Lab) (SU)	Sulfate (mg/L)
7/7/2024	110	<4	36	39	120	<10				7.53	
7/24/2024			19	24	170	<10	51	12	9.6	6.9	<6
8/3/2024	250	<4	16	19	210	<10				7.35	
8/7/2024			18	22	190	<10	56	12	11	8.17	3.4
9/3/2024	190	<4	19	22	150	<10				7.41	
10/2/2024			20	27	150	<10	44	11	8.1	7.54	<6
10/16/2024			220	47	110	<10	29	9.7	5.9		<6
10/28/2024	120	<4	26	35	140	<10				7.55	
11/4/2024	120	5	36	41	91	<10				7.69	
12/1/2024	140	<4	33	41	100	<10				7.69	
1/5/2025	100	<4	36	44	88	<10				7.48	
4/7/2025	85	4	57	59	62	<10				7.45	
5/5/2025	130	14	73	110	74	<10				7.63	
5/20/2025	160	43	38	96							
6/2/2025	160	37	18	38	150	<10				7.64	
7/24/2025	160	15	34	54							
8/3/2025	180	30	22	55	170	<10				7.98	
9/1/2025	230	4	10	14	180	<10				7.5	
10/5/2025	190	6.3	12	21	170	<10				7.31	
11/2/2025	200	<4	19	26	170	<10				7.59	
12/7/2025	160	<4	25	37	120	<10				7.64	
5/4/2026				89							
5/12/2026	120	<4	48	62	110	<10				7.92	
6/1/2026	180	<4	9.7	31	150	<10				7.74	

Notes

Prepared by: KRM2, LDC

Checked by: DCF1

1. Blank cells represent an analyte not tested during that event.

2. Significant figures are as reported from the database obtained from White Pine Copper.

mg/L = milligram per liter

µg/L = microgram per liter

Appendix Table I.1-9
Surface Water Quality - South Dam
White Pine Copper LLC

Detected Analytes				
Date	Total Suspended Solids (mg/L)	Chloride (mg/L)	Total Recoverable Copper (µg/L)	Dissolved Copper (µg/L)
1/8/2006	<4		31	27
2/12/2006	<4		41	30
3/12/2006	<4		33	22
4/9/2006	<4		38	32
5/7/2006	<4		48	39
6/11/2006	<4		43	35
4/8/2007	<4		43	35
5/13/2007	4		21	20
6/10/2007	<4		18	19
10/14/2007	<4		32	27
4/13/2008	24		45	31
5/11/2008	27		30	26
4/12/2009	<4		23	20
5/10/2009	6		23	21
6/14/2009	8		27	20
10/11/2009	4		5	5
11/8/2009	4		10	10
3/14/2010	6		42	30
4/11/2010	4		14	13
5/9/2010	4		17	16
10/10/2010	4		11	9
11/14/2010	4		10	8
5/8/2011	4		18	18
11/13/2011	5		11	8
3/11/2012	4		12	9
4/8/2012	4		7	9
7/8/2012	4		5	5
8/12/2012	4		6	5
9/9/2012	4		5	5
11/11/2012	4		6	6
4/14/2013	4		30	25
5/12/2013	4		20	16
6/9/2013	5		11	11
7/14/2013	4		8	6
8/11/2013	4		5	5
9/8/2013	8		5	5
10/13/2013	4		9	6
11/10/2013	8		9	15
4/13/2014	4		25	18
5/11/2014	4		33	24
6/8/2014	4		8	8
7/13/2014	4		12	8
8/10/2014	4		5	5
9/14/2014	8		8	12
10/12/2014	4		20	5
11/9/2014	4		5	5

Table I.1-9 (continued)

Detected Analytes				
Date	Total Suspended Solids (mg/L)	Chloride (mg/L)	Total Recoverable Copper (µg/L)	Dissolved Copper (µg/L)
12/14/2014	4		13	13
4/12/2015	4		13	12
5/10/2015	4		14	14
6/14/2015	4		7	8
7/12/2015	4		8	7
8/9/2015	4		11	10
9/13/2015	4		6	5
10/11/2015	4		7	7
11/8/2015	4		5	5
12/13/2015	4		6	7
3/13/2016	4	10	14	10
4/10/2016	4	10	13	12
5/8/2016	4	10	11	11
6/12/2016	4	10	6	5
7/10/2016	20	10	5	5
8/14/2016	4		4	2
9/11/2016	4	10	3	2
10/9/2016	6	12	4	3
11/13/2016	4	11	4	4
4/9/2017	4	10	9	4
5/8/2017	4	10	12	10
6/11/2017	4	10	9	8
7/9/2017	4	10	6	4
8/13/2017	4	10	3	
9/10/2017	8	10	3	3
10/8/2017	4	10	3	2
5/13/2018	4	10	9	6
6/10/2018	4	10	8	6
7/8/2018	4	10	5	4
8/12/2018	4	10	3	2
9/9/2018	4		2	2
10/14/2018	4		5	5
11/11/2018	4	10	5	4
4/15/2019	4	10	17	13
5/13/2019	4	10	10	10
6/9/2019	14	10	13	8
4/13/2020	5	10	13	11
5/11/2020	4	10	7	6
6/7/2020	4	10	4	4
7/12/2020	14	10	2	2
8/9/2020	6	10	2	1
9/13/2020	4	10	4	2
10/11/2020	4	10	4	3
11/8/2020	5	10	4	3
3/14/2021	4	10	8	6
3/14/2021	<4.0	<10		6
4/12/2021	4	10	6	6
4/12/2021	4	<10		6
5/10/2021	4	10	5	6

Table I.1-9 (continued)

Detected Analytes				
Date	Total Suspended Solids (mg/L)	Chloride (mg/L)	Total Recoverable Copper (µg/L)	Dissolved Copper (µg/L)
5/10/2021	<4.0	<10		6
6/14/2021	4	10	3	3
6/14/2021	<4.0	<10		3
7/11/2021	10	10	8	5
7/11/2021	10	<10		5
8/8/2021	6	10	10	3
8/8/2021	6	<10		3
10/10/2021	4	16	4	2
10/10/2021	<4.0	16		2
11/14/2021	4	10	3	3
11/14/2021	<4.0	<10		3
4/11/2022	4	10	17	16
4/11/2022	<4.0	<10		16
5/9/2022	4	10	10	9
5/9/2022	<4.0	<10		9
6/13/2022	4	10	6	5
6/13/2022	<4.0	<10		5
7/11/2022	4	<10	2	2
8/14/2022	5	<10	1	<1
9/12/2022	<4	<10	<1	<1
10/9/2022	<4	<10	2	1
11/13/2022	<4	<10	5	5
12/11/2022	<4	<10	6	6
4/9/2023	<4	<10	9	8
5/8/2023	<4	<10	13	13
6/11/2023	<4	<10	4	3
7/9/2023	18	<10	4	2
11/12/2023	<4	<10	9	7
2/11/2024	<4	<10	4	3
3/11/2024	<4	11	3	3
4/15/2024	<4	<10	5	4
5/13/2024	<4	<10	6	6
6/9/2024	<4.0	<10	4	3
6/9/2024	<4	<10	4	3

Prepared by: KRM2, LDC

Checked by: DCF1

Notes:

1. Blank cells represent an analyte not tested during that event.
2. Sample of Total Dissolved Solids (72 mg/L) taken on 8/13/2017 was excluded from table due to limited data.
3. Significant figures are as reported from the database obtained from White Pine Copper.

mg/L = milligram per liter

µg/L = microgram per liter

Appendix Table I.1-9a
Surface Water Quality - South Dam
White Pine Copper LLC

Detected Analytes				
Date	Total Suspended Solids (mg/L)	Chloride (mg/L)	Total Recoverable Copper (µg/L)	Dissolved Copper (µg/L)
7/14/2024	<4.0	<10	4.3	3.8
8/11/2024	<4.0	<10	4.1	2.8
9/10/2024	4	<10	3.3	2.1
10/15/2024	5.9	<10	3	2.4
11/12/2024	<4.0	<10	5.8	1.9
3/10/2025	<4.0	<10	5.3	2.7
4/13/2025	<4.0	<10	11	9.8
5/12/2025	<4.0	<10	12	8.8
6/8/2025	13	<10	16	8.3
7/13/2025	4	<10	4.7	<5.0
8/10/2025	<4.0	<10	5	3.8
9/7/2025	<4.0	<10	2.3	1.8
10/12/2025	<4.0	<10	3.9	3
11/9/2025	<4.2	<10	2.8	3.3
5/12/2026	4.6	<10	16	4.6
6/7/2026	4.7	<10	23	4.7

Prepared by: KRM2, LDC

Checked by: DCF1

Notes:

1. Blank cells represent an analyte not tested during that event.

2. Significant figures are as reported from the database obtained from White Pine Copper.

mg/L = milligram per liter

µg/L = microgram per liter

Appendix Table I.1-10
Surface Water Quality - Subterra Underground Discharge
White Pine Copper LLC

	Detected Analytes						
Date	Total Dissolved Solids (mg/L)	Chloride (mg/L)	Hardness (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (mg/L)	pH (Lab) (SU)	Total Suspended Solids (mg/L)
10/28/2012	2500		750	53	110	7.55	<4
11/4/2012	2900		730	15	98	7.48	<4
11/11/2012	2700	1100	840	25	100	7.45	<4
11/18/2012	2800	940	740	9.4	110	7.28	<5
11/25/2012	2900	880	570	120	140	7.23	<4
12/2/2012	5100	870	740	81	91	7.47	<4
1/13/2013	2400	860	290	21	120	7.29	<4
1/27/2013	2600	970	610	54	98	7.32	<4
2/3/2013	2700	970	540	9.9	99	7.33	<4
2/10/2013	2700	970	620	30	110	7.26	<4
2/17/2013	2300	900	490	30	120	7.26	<4
2/24/2013	9800	910	800	30	130	7.5	<4
3/17/2013	5100	990	820	20	110	7.31	<4
3/24/2013	2500	970	820	14	110	7.29	<4
4/14/2013	2700	880	800	20	100	7.68	<4
4/21/2013	2600	940	720	16	120	7.4	<4
4/28/2013	2900	920	930	26	120	7.45	<4
5/5/2013	2300	820	1100	87	160	7.4	<4
5/12/2013	2900	860	1100	68	140	7.55	<4
5/19/2013	2800	970	720	81	140	7.51	<4
5/27/2013	2600	850	660	79	140	7.39	5
6/9/2013				110	140		<4
6/16/2013	2500	810	800	99	150	7.46	<4
6/30/2013	2900	960	700	100	200	7.31	4
7/7/2013		900	700	62	120	7.53	<4
8/4/2013	1500	870	720	62	130	7.7	6
8/11/2013	3000	850	770	67	140	7.33	<4
9/2/2013	3000	970	1400	100	190	7.5	<4
9/8/2013	3000	810	750	68	160	7.47	9
9/15/2013	2800	890	670	79	150	7.57	<4
10/6/2013	2900	870	700	29	130	7.57	<4
10/13/2013	2700	870	680	64	150	7.5	4
11/25/2013	2400	910	970	<5.2	17	7.48	<4
12/1/2013	2500	920	780	140	120	7.5	<4
12/8/2013	2400	930	840	50	140	7.55	<4
12/15/2013	2400	960	780	150	120	7.53	<4
1/4/2014	2700	1300	750	33	110	7.52	<4
4/6/2014	2800	1100	720	14	78	7.23	13
4/13/2014	3100	1100	930	8.8	94	7.19	<4
5/4/2014	3100	1000	740	51	170	7.43	5
5/11/2014	2900	1000	690	58	160	7.4	<4

Table I.1-10 (continued)

	Detected Analytes						
Date	Total Dissolved Solids (mg/L)	Chloride (mg/L)	Hardness (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (mg/L)	pH (Lab) (SU)	Total Suspended Solids (mg/L)
6/8/2014	2900	940	610	70	120	7.44	11
6/15/2014	3100	940	830	70	150	7.48	8
6/22/2014	2700	1000	650	72	130	7.39	6
6/29/2014	3100	930	650	83	130	7.43	<20
7/6/2014	3100	950	670	73	130	7.67	4
7/13/2014	2800	840	660	71	130	7.34	6
7/27/2014	2200	930	700	62	130	7.3	7
8/3/2014	3200	910	660	63	130	7.46	20
8/10/2014	3200	900	650	61	120	7.61	5
8/17/2014	2500	880	670	65	130	7.58	7
10/5/2014	2300	1000	810	55	130	7.44	<4
10/12/2014	3200	1100	860	48	130	7.42	5
10/19/2014			760	51	120	7.36	4
11/2/2014	2600	1100	780	44	130	7.59	5
11/9/2014	2200	10000	780	59	130	7.67	5
11/17/2014	2500	950	860	48	130	7.4	<4
12/14/2014	2200	1500	780	21	110	7.51	<4
12/21/2014	2900	1100	720	37	110	7.96	<16
1/12/2015	2600	1200	970	36	130	7.57	<4
1/18/2015	14000	1100	810	44	120	7.6	<4
2/1/2015	2800	1100	810	53	120	7.68	6
2/8/2015	2400	1500	690	79	140	7.85	62
3/15/2015	2700	1200	460	31	100	7.45	7.5
3/22/2015	2600	2200	810	36	120	7.58	16
3/29/2015	2800	1200	880	15	110	7.51	7
4/3/2015	2800	1100	730	40	130	7.59	<4
4/6/2015	3000	1200	740	52	130	7.57	4
4/12/2015	2800	1100	750	71	130	7.74	<4
4/19/2015	2700	1200	770	67	140	7.58	<20
4/26/2015	2900	1000	810	110	170	7.78	<4
5/3/2015	6700	1100	900	68	170	7.54	9
5/10/2015	3000	1000	630	97	130	7.55	<4
5/17/2015	2800	1000	690	80	120	7.62	<4
6/30/2015	3000	1100	720	71	140	7.57	8
7/5/2015	3100	1000	820	68	140	7.51	<4
7/12/2015	3000	1100	770	58	140	7.52	5
7/19/2015	2900	1000	790	73	130	7.55	6
7/26/2015	3200	1000	870	64	160	7.55	<4
8/2/2015	3100	1000	790	57	140	7.54	5
8/16/2015	2900	1100	750	63	130	7.58	<16
10/11/2015	2800	1100	660	27	110	7.44	<4
10/18/2015	2700	1100	780	41	120	7.57	<16
10/25/2015	2800	1100	710	44	130	7.55	<4
11/1/2015	2700	1100	720	26	100	7.5	<4
11/8/2015	2600	1100	730	31	120	7.57	6

Table I.1-10 (continued)

	Detected Analytes						
Date	Total Dissolved Solids (mg/L)	Chloride (mg/L)	Hardness (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (mg/L)	pH (Lab) (SU)	Total Suspended Solids (mg/L)
12/20/2015	2700	1100	1000	19	100	7.46	<4
12/27/2015	2800	1100	730	38	120	7.49	<4
1/3/2016	2600	1200	750	19	98	7.45	<4
1/17/2016		1100	770	45	130	7.61	<4
1/24/2016	2700	1200	750	5.5	81	7.58	<4
2/8/2016	2700	1200	840	5.2	77	7.47	8
2/15/2016	2500	1200	810	5.2	80	7.47	7
3/13/2016	2800	1200	680	23	90	7.45	<4
3/20/2016	3000	1200	880	97	94	7.5	5
3/28/2016	2900	1200	790	20	110	7.47	<4
4/1/2016	2700	1200	700	63	130	7.62	<4
4/4/2016	2800	1100	730	54	130	7.51	<4
4/17/2016	2800	1100	720	27	110	7.47	<4
4/24/2016	2800	1100	740	62	130	7.66	<4
6/26/2016	3000	1100	710	41	130	7.49	<4
7/4/2016	2800	1100	740	52	140	7.55	<4
7/10/2016	3100	1100	760	53	130	7.53	7
7/24/2016	2900	1400	760	44	140	7.49	6
7/31/2016	2500	950	630	52	150	7.53	4
8/7/2016	2900	930	660	39	140	7.53	4
8/14/2016	2000	930	630	43	140	7.54	<4
8/22/2016	2700	1400	710	48	160	7.5	5
8/28/2016	2800	1100	710	41	140	7.46	<4
9/18/2016	2300	980	660	39	140	7.52	<4
9/25/2016		960	690	29	120	7.55	<4
10/2/2016	2400	1100	720	27	120	7.57	<4
10/9/2016	2800	890	750	23	100	7.49	8
10/16/2016	2600	980	740	30	110	7.45	<4
10/23/2016	2700	1000	570	27	110	7.48	<4
10/30/2016	2700	1100	740	54	120	7.56	6
11/6/2016	2700	1900	740	24	100	7.53	4
11/13/2016	3000	1100	560	34	110	7.57	<4
11/20/2016	3000	1200	810	23	85	7.41	<8
11/28/2016	2600	1400	770	4.8	72		<4
12/4/2016	2300	1100	730	6.9	90	7.44	<8
12/11/2016	2200	1100	720	28	120	7.51	<4
12/19/2016	2300	1200	720	28	86	7.47	4
12/26/2016	2800	1000	720	27	74	7.45	<4
1/2/2017	2300	1200	920	18	84	7.45	<4
1/8/2017	2300	1200	830	7.5	64	7.33	<8
2/5/2017	2400	1200	870	1	53	7.45	<4
2/12/2017	2600	1300	880	1.9	49	7.57	<5.3
2/19/2017	2600	1600	830	1	49	7.43	4
2/26/2017	2700	1400	890	2.1	63		5
3/5/2017	2700	1500	850	2.2	83	7.43	5

Table I.1-10 (continued)

	Detected Analytes						
Date	Total Dissolved Solids (mg/L)	Chloride (mg/L)	Hardness (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (mg/L)	pH (Lab) (SU)	Total Suspended Solids (mg/L)
3/13/2017	2600	1200	780	5.1	93	7.46	<4
3/20/2017	2900	1300	780	7.9	95	7.52	4
3/27/2017	2900	1200	870	11	100	7.62	<4
4/1/2017	3100	1200	790	69	160	7.51	<4
4/9/2017	2900	1200	710	11	99	7.55	<4
4/17/2017	2700	1300	840	23	98	7.52	4
4/24/2017	3200	1300	840	40	100	7.48	4
5/8/2017	3300	1300	720	63	120	7.54	<4
5/15/2017	2600	1200	750	55	120	7.5	<4
5/22/2017	2700	1100	650	81	140	7.52	<4
5/29/2017	2700	1100	730	79	130	7.5	<4
6/18/2017	2600	1100	690	62	120	7.48	<4
7/2/2017	2900	1100	830	65	130	7.48	<4
7/9/2017	3000	1100	620	66	120	7.53	<4
7/16/2017	3100	1100	730	61	130	7.6	<4
7/23/2017	3000	1100	810	38	100	7.69	4
7/30/2017	3100	1200	840	45	130	7.68	<4
8/6/2017	3000	1200	820	43	120	7.56	<4
8/13/2017	3000	1100	780	38	120	7.69	<4
8/21/2017	2700	1100	820	33	110	7.52	<4
9/4/2017	3400	1200	710	24	94	7.68	<4
9/10/2017	3200	1200	810	22	97	7.43	<4
9/24/2017	3200	1200	730	23	100	7.22	<4
10/1/2017	3300	1200	850	32	100	7.49	<4
10/8/2017	3200	1300	800	19	93	7.43	<4
10/15/2017	3300	1500	940	7.7	91	7.12	<4
10/22/2017	3200	1200	910	18	88	7.35	<4
11/5/2017	2800	1300	880	2.7	64	7.62	5
11/12/2017	2600	1200	850	16	70	7.39	<4
11/19/2017	2900	1200	880	16		7.62	<4
11/25/2017	2700	1200	810	16	77	7.48	<4
12/3/2017	2700	1300	900	2.8	69	7.44	<4
12/10/2017	2500	1200	960	4.5	64	7.56	<4
12/17/2017	2600	1300	900	7.3	74	7.37	<4
12/25/2017	2600	1500	970	6.9	78	7.56	<4
1/8/2018	2700	1300	920	16	84	7.6	<4
1/14/2018	2900	1300	910	15	78	7.56	4
1/21/2018	3200	1300	950	27	94	7.57	<4
2/4/2018	2600	1300	840	32	94	7.55	<4
2/11/2018	2900	1300	860	33	92	7.54	<4
3/12/2018	2700	1300	1000	28	110	7.55	<4
3/19/2018	2600	1300	930	110	90	7.35	<4
3/26/2018	2700	1300	890	25	64	7.37	4
4/2/2018	2800	1300	890	21	70	7.49	<4
4/8/2018	3100	1400	910	20	91	7.49	6

Table I.1-10 (continued)

	Detected Analytes						
Date	Total Dissolved Solids (mg/L)	Chloride (mg/L)	Hardness (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (mg/L)	pH (Lab) (SU)	Total Suspended Solids (mg/L)
4/16/2018	3000	1400	1000	17	99	7.41	<4
4/22/2018	2800	1400	950	15	82	7.53	<4
4/30/2018	3200	1200	930	24	110	7.56	<4
5/7/2018	3200	1200	940	34	120	7.28	4
5/13/2018	3100	1200	930	20	130	7.4	<4
5/21/2018	3000	1200	900	40	130	7.56	5
6/3/2018	3100	1200	810	42	140	7.55	<4
6/10/2018	3300	1300	910	36	130	7.44	<4
6/24/2018	3200	1200	830	70	130	7.26	<4
7/8/2018	3000	1100	800	36	130	7.48	<4
7/15/2018	3200	1200	810	38	76	7.54	<4
7/22/2018	3300	1200	830	36	110	7.28	<4
7/29/2018	3400	1300	860	35	190	7.38	<4
8/5/2018	3500	130	210	34	110	7.23	4
9/16/2018	2900	1500	830	85	120	7.45	24
9/30/2018	3500	1200	790	4.1	85	7.58	6
10/7/2018	3500	1600	900	2	61	7.36	<4
10/14/2018	3400	1400	280	20	50	7.3	8
10/28/2018	2600	1300	180	5.3	73	7.52	8
12/2/2018	2700	150	900	11	90	7.46	<4
12/9/2018		1300	900	32	94	7.69	
12/16/2018	3100	1300	930	3.3	91	7.68	4
12/24/2018	3100	1600	880	1	46	7.3	8
12/31/2018	2800	1300	740	2	61	7.51	4
1/6/2019	2700	1500	870	6.6	90	7.31	<4
1/13/2019	2500	1400	650	11	81		<4
1/20/2019	2600	1300	830	29	100	7.53	<4
1/28/2019	2900	1300	790	32	97	7.42	<4
3/25/2019	3200	1300	860	23	93	7.11	5
3/31/2019	2700	1400	860	6.3	82	7.23	<4
4/8/2019	3300	1400	890	1	65	7.19	9
4/15/2019	3200	1400	880	5.4	78	7.22	<4
4/22/2019	2900	1200	880	37	130	7.34	6
4/29/2019	2800	1200	820	50	100	7.06	<4
5/6/2019	5100	1200	790	73	140	7.54	<4
5/13/2019	3000	1200	800	61	120	7.69	7
5/20/2019	3200	1200	740	67	120	7.6	<4
5/27/2019	2700	1200	910	75	140	7.67	8
6/16/2019	3000	1100	870	35	120	7.56	5
6/23/2019	3000	110	770	69	130	7.41	<4
7/7/2019	3000	1100	740	65	130	7.31	<4
7/14/2019	2900	1100	960	45	130	7.02	<4
7/21/2019	3100	1100	800	42	130	7.43	10
7/28/2019				22	110		
8/4/2019	3100	1100	690	42	130	7.55	<4

Table I.1-10 (continued)

	Detected Analytes						
Date	Total Dissolved Solids (mg/L)	Chloride (mg/L)	Hardness (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (mg/L)	pH (Lab) (SU)	Total Suspended Solids (mg/L)
8/11/2019	3200	1100	740	39	78	7.56	<4
8/18/2019	3000	1100	700	35	110	7.69	6
8/25/2019	3000	1100	740	3.9	110	7.64	12
9/2/2019	3300	1200	740	23	110	7.56	<4
11/3/2019	2400	1100	720	36	130	7.5	<4
11/10/2019	2500	1200	770	7	93	7.31	<4
11/17/2019	3100	1200	850	53	82	7.5	<4
11/24/2019	2500	1300	800	6.3	74	7.54	<4
12/1/2019	2700	1200	850	16	83	7.62	7
12/8/2019	2500	1300	880	20	44	7.72	14
12/16/2019	2900	1200	910	1.7	61	7.81	4
12/22/2019	2700	1200	850	16	64	7.71	<4
12/29/2019	2700	1200	870	32	61	7.45	9
1/5/2020	3100	1300	860	12	65	7.24	7
1/12/2020	2700	740	870	25	59	7.64	<4
1/20/2020	2900	1300	910	4.7	66	7.02	5
1/26/2020	2700	1200	880	7.9	88	7.65	10
4/6/2020	3200	1400	920	6.4	36	7.44	<4
4/13/2020	2900	1500	910	10	51	7.22	11
4/20/2020	3300	1500	910	14	58	7.54	5
4/27/2020	2900	1300	840	34	100	7.62	7
5/4/2020	2600	1300	800	55	110	7.66	<4
5/11/2020	3200	1200	790	48	140	7.16	4
5/18/2020	3200	1200	810	86	140	7.43	5
5/25/2020	3200	1200	810	74	120	6.89	<4
6/1/2020	3100	1200	800	51	110	7.58	<4
6/7/2020	3200	1200	810	55	120	7.3	4
6/14/2020	3100	560	850	49	120	7.11	4
6/21/2020	3200	1200	790	39	110	7.21	4
7/5/2020	3500	1200	790	50	120	7.16	<4
7/12/2020	2300	1200	780	66	110	7.57	<4
7/26/2020	3300	1200	760	39	120	7.56	4
8/2/2020	3300	1300	810	38	120	7.71	<4
8/9/2020	3000	1200	800	47	110	7.11	<4
9/4/2020	2900	1600	850	18	70	7.51	6
9/7/2020	3100	1300	760	29	100	7.46	6
9/13/2020	3000	1300	790	23	100	6.82	<4
9/20/2020	3100	1300	920	11	81	7.48	<9
10/18/2020	3500	1300	910	6.2	70	6.8	<4
12/6/2020	3000	1400	1000	5.1	55	7.53	4
12/13/2020	2100	1400	950	1.6	57	7.44	5
1/3/2021	3300	1300	1000	4	47	7.61	6
1/10/2021	2400	1200	880	17	98	7.49	<4
1/17/2021	2300	1100	800	43	110	7.55	6
1/24/2021	2300	1200	800	17	80	7.61	13

Table I.1-10 (continued)

	Detected Analytes						
Date	Total Dissolved Solids (mg/L)	Chloride (mg/L)	Hardness (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (mg/L)	pH (Lab) (SU)	Total Suspended Solids (mg/L)
1/31/2021	2700	1200	730	49	100	7.51	<4
3/29/2021	3300	130	850	14	8	7.54	10
4/4/2021	3200	1300	890	40	70	7.56	<4
4/12/2021	2900	1200	900	34	120	7.57	<4
4/18/2021	2700	1100	850	45	150	7.55	4
4/26/2021	2900	1200	830	23	78	7.55	4
5/3/2021	3000	1200	830	34	110	7.55	<4
5/10/2021	3200	1200	210	42	100	7.55	14
5/17/2021	3300	1200	840	92	75	7.48	6
5/24/2021	3400	1300	870	22	90	7.59	<4
5/31/2021	3500	1300	910	17	100	7.52	5
6/7/2021	3600	1300	860	46	63	7.33	<4
6/14/2021	3800	1600	940	16	71	7.51	6
6/20/2021	3200	1300	1000	16	88	7.56	8
6/27/2021	3000	1300	960	4.8	67	7.36	4
7/18/2021	4000	1300	880	12	70	7.39	<4
6/27/2022	3000	1100	770	34	82	7.29	<4
7/3/2022	3000	1200	190	65	120	7.53	4
7/11/2022	3000	1000	710	72	120	7.52	8
7/18/2022	2700	2200	140	72	120	7.36	<4
7/25/2022	2800	1100	810	83	140	7.56	<4
7/31/2022	3000	1100	770	69	120	7.63	<4
11/6/2022	2800	1100	820	46	110	7.5	<4
11/13/2022	2800	1100	830	70	81	7.45	4
11/20/2022	3000	1100	810	44	120	7.33	4
11/27/2022	2700	1200	780	46	120	7.24	<4
3/6/2023	2600	1300	950	70	140	7.47	<4
3/13/2023	2300	1400	970	25	120	7.33	<4
3/20/2023	2900	1300	880	30	<1.2	7.23	<4
3/27/2023	2800	1300	920	34	120	7.55	<4
4/1/2023	2700	1100	880	45	150	7.24	<4
4/3/2023	3100	1300	1000	25	120	7.27	<4
4/9/2023	3300	1300	980	23	110	7.29	<4
4/19/2023	3000			12	.		<4
4/24/2023	2600	1200	820	23	100	7.19	<4
5/8/2023	2400	1200	850	21	83	6.93	<4
5/15/2023	3000	1200	880	62	140	7.53	<4
5/22/2023	2400	1100	850	47	150	6.56	<4
5/29/2023	2900	1200	820	36	14	6.64	<4
6/5/2023	2900	1200	830	31	86	7.24	<4
6/11/2023	2700	1200	800	31	140	6.63	<4
6/18/2023	2900	1200	860	48	140	7.68	<4
6/25/2023	3100	1200	830	51	140	7.37	<4
7/4/2023	3000	1200	820	42	75	7.64	4
7/9/2023	2700	1200	780	42	150	7.43	<4

Table I.1-10 (continued)

	Detected Analytes						
Date	Total Dissolved Solids (mg/L)	Chloride (mg/L)	Hardness (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (mg/L)	pH (Lab) (SU)	Total Suspended Solids (mg/L)
7/16/2023	3000	1100	810	52	83	7.23	<4
7/17/2023	3000			48	83		<4
7/23/2023	2600	1100	810	44	140	7.57	<4
7/30/2023	2800	1100	790	45	110	7.49	<4
1/7/2024	2700	1100	770	41	150	7.41	<4
1/14/2024		1100		26	120	7.76	<4
1/21/2024	2800	1200	940	18	100	7.76	<4
1/28/2024	3100	1300			66		5
2/4/2024	3100	1400	990	18	110	7.25	<4
2/11/2024	3000	1400	1000	7.3	68	7.3	<4
2/18/2024	2900	1400	930	14	80	7.05	<4
2/25/2024	2900	1400	1000	25	58	7.36	4
3/4/2024	3700	1400	960	9.3	75	7.3	<
3/11/2024	3000	1500	780	7.9	70	7.43	<
3/18/2024	3200	1400	900	25	86	7.46	<
3/23/2024	3100			24	92		<
4/7/2025	3300	1300	1100	<25	63	7.3	4
4/13/2025	3900	1400	990	<1.0	24	7.2	4
4/21/2025	3600	1400	1100	14	79	7.44	6
4/28/2025	3500	1500	1100	15	110	7.27	4
5/5/2025	3200	1600	1100	11	86	7.36	4
5/12/2025	4000	1600	220	21	99	7.4	6
5/19/2025	3900	1500	1100	20	55	7.38	<4.3
5/20/2025	2600			27	52		8.1
5/26/2025	3400	1600	1100	21	100	7.32	7.3
6/2/2025	3900	1500	1200	25	91	7.36	4
6/8/2025	3500	1500	1100	21	98	7.46	<4.0
6/15/2025	3800	1500	1100	19	83	7.29	4
6/17/2025	4000			20	99		5
6/22/2025	4100	1500	4000	17	360	7.45	4

Notes:

Prepared by: KRM2, LDC

1. Blank cells represent an analyte not tested during that event.

Checked by: DCF1

2. Significant figures are as reported from the database obtained from White Pine Copper.

mg/L = milligram per liter

µg/L = microgram per liter

Appendix Table I.1-11
Surface Water Quality - Tailings: North Pond #1 - Historical
White Pine Copper LLC

Detected Analytes				
Date	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Chloride (mg/L)
01/08/2006	<4	37	50	
02/12/2006	<4	46	52	
03/12/2006	<4	34	46	
04/09/2006	<4	41	10	
05/07/2006	13	42	16	
06/11/2006	10	56	66	
07/09/2006	9	22	52	
08/13/2006	58	22	16	
10/08/2006	49	26	11	
11/12/2006	16	15	57	
12/10/2006	<4	12	15	
01/14/2007	<4	41	49	
02/11/2007	4	29	33	
03/11/2007	<4	36	43	
04/08/2007	32	71	280	
05/13/2007	11	40	93	
06/10/2007	18	22	64	
07/08/2007	9	20	46	
10/14/2007	43	18	100	
12/09/2007	5	38	48	
02/09/2008	<4	56	63	
04/13/2008	7	57	95	
05/11/2008	20	44	140	
10/12/2008	11	17	32	
02/08/2009	<4	24	42	
03/08/2009	5	60	71	
04/12/2009	10	39	84	
05/10/2009	14	43	88	
06/14/2009	14	20	51	
09/13/2009	4	31	36	
10/11/2009	53	29	150	
11/08/2009	22	32	90	
02/14/2010	<4	47	55	
03/14/2010	7	41	69	
04/11/2010	23	26	100	
05/09/2010	9	17	32	

Table I.1-11 (continued)

Detected Analytes				
Date	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Chloride (mg/L)
07/11/2010	<4	22	33	
08/08/2010	7	16	29	
09/12/2010	68	22	98	
10/10/2010	17	7	33	
11/14/2010	10	11	31	
12/14/2010	<4	20	23	
01/09/2011	<4	39	39	
05/08/2011	6	32	72	
06/12/2011	4	39	80	
07/10/2011	<4	19	31	
08/14/2011	4	17	34	
09/11/2011	7	36	61	
10/09/2011	14	6.3	31	
11/13/2011	74	18	140	
12/11/2011	7	12	35	
02/12/2012	<4	33	37	
03/11/2012	5	45	50	
04/08/2012	<4	26	68	
07/08/2012	5	16	23	
08/12/2012	<4	20	31	
09/09/2012	7	7.7	26	
10/14/2012	16	9.3	17	
11/11/2012	39	29	130	
12/09/2012	<4	32	45	
01/13/2013	<4	39	44	
02/10/2013	<4	44	48	
03/10/2013	<4	23	32	
04/14/2013	<4	39	60	
05/12/2013	52	110	240	
06/09/2013	7	38	54	
07/14/2013	5	33	48	
08/11/2013	10	16	32	
09/08/2013	15	8.3	26	
10/13/2013	5	13	36	
11/10/2013	20	23	150	
12/08/2013	<4	56	61	
04/13/2014	18	41	89	
05/11/2014	19	49	160	
06/08/2014	<4	41	51	
07/13/2014	10	19	28	
08/10/2014	6	16	23	

Table I.1-11 (continued)

Detected Analytes				
Date	Total Suspended Solids (mg/L)	Dissolved Copper (μg/L)	Total Recoverable Copper (μg/L)	Chloride (mg/L)
09/14/2014	30	120	120	
10/12/2014	160	17	180	
11/09/2014	32	28	75	
12/14/2014	<4	39	41	
01/12/2015	<4	49	43	
02/09/2015	4	27	34	
04/12/2015	64	29	150	
05/10/2015	21	16	41	
06/14/2015	6	15	28	
07/12/2015	<4	24	29	
08/09/2015	8	21	30	
09/13/2015	17	15	48	
10/11/2015	55	23	100	
11/08/2015	74	30	130	
12/13/2015	<4	18	19	
01/10/2016	<4	28	37	130
03/13/2016	<4	16	20	15
04/10/2016	<4	23	34	140
05/08/2016	4	23	48	200
06/12/2016	9	25	43	210
07/10/2016	<4	19	28	250
08/14/2016	5	11	29	
09/11/2016	5	28	59	380
10/09/2016	6	17	30	310
11/13/2016	28	27	96	550
12/11/2016	8	32	63	390
01/08/2017	<4	40	43	400
02/12/2017	<4	24	29	170
03/13/2017	<4	30	45	58
04/09/2017	16	21	77	250
05/08/2017	6	34	61	170
06/11/2017	13	25	130	180
07/09/2017	<4	14	26	260
08/13/2017	<4		18	450
09/10/2017	<4	33	46	400
10/08/2017	4	17	30	340
11/12/2017	<4	28	40	240
12/10/2017	<4	25	38	270
01/08/2018	<4	23	30	230
02/11/2018	<4	7.9	19	280
03/12/2018	<4	6.8	19	400

Table I.1-11 (continued)

Detected Analytes				
Date	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Chloride (mg/L)
04/08/2018		13	26	320
05/13/2018	<4	15	36	220
06/10/2018	13	7.2	24	410
07/08/2018	14	15	54	400
08/12/2018	<4	13	21	490
09/09/2018	4	14	37	
10/14/2018	9	27	45	
11/11/2018	5	19	32	270
12/09/2018	<4	24	23	80
01/13/2019	<4	66	23	220
04/15/2019	<4	26	69	55
05/13/2019	5	30	44	170
06/09/2019	<4	24	28	200
07/14/2019	<4	16	21	290
08/11/2019	<4	18	20	500
09/08/2019	<4	24	20	
10/13/2019	5	20	32	570
11/10/2019	<4	20	31	
12/08/2019	<4	17	21	260
03/09/2020	<4	7.9	16	210
04/13/2020	4	20	38	64
05/11/2020	<4	13	27	250
06/07/2020	4	22	26	370
07/12/2020	<4	19	23	360
08/09/2020	<4	19	22	490
09/13/2020	<4	12	18	670
10/11/2020	7	11	18	710
11/08/2020	19	16	29	520
12/13/2020	<4	20	24	410
01/10/2021	<4	29	29	450
03/14/2021	4	23		26
04/12/2021	9	19	43	210
05/10/2021	<4	18	28	300
06/14/2021	9	11	14	470
07/11/2021	<4	16	19	780
08/08/2021	7	17	24	750
10/10/2021	<4	19	39	960
11/14/2021	9	30	53	590
12/12/2021	4	29	130	670
04/11/2022	6	32	62	53
05/09/2022	8	33	75	92

Table I.1-11 (continued)

Detected Analytes				
Date	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Chloride (mg/L)
06/13/2022	<4	27	34	80
07/11/2022	<4	25	26	150
08/14/2022	<4	20	22	340
09/12/2022	5	16	16	370
10/09/2022	<4	17	17	350
11/13/2022	12	35	83	130
12/11/2022	<4	24	27	83
01/08/2023	<4	20	20	140
02/12/2023	<4	11	19	200
04/09/2023	<4	20	27	70
05/08/2023	15	29	58	80
06/11/2023	4	15	21	160
07/09/2023	<4	14	15	290
08/13/2023	<4	18	14	560
11/12/2023	<4	17	24	630
12/10/2023	<4	21	20	710
01/14/2024	<4	32	45	380
02/11/2024	5	39	71	220
03/11/2024	5	31	43	380
04/15/2024	4	25	34	320
05/13/2024	<4	24	30	270
06/09/2024	<4.0	19	25	290

Notes:

Prepared by: DCF1

1. Sample taken 8/13/2017 for Total Dissolved Solids (1300 mg/L) was excluded from the table due to lack of data.

Checked by: MAN

2. Blank cells represent an analyte not tested during that event.

3. Significant figures are as reported from the database obtained from White Pine Copper.

mg/L = milligram per liter

µg/L = microgram per liter

Appendix Table I.1-11a
Surface Water Quality - Tailings: North Pond 1 (2024-2026)
White Pine Copper LLC

Detected Analytes				
Date	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Chloride (mg/L)
07/14/2024	<4.0	25	25	140
08/11/2024	<4.0	14	17	170
09/10/2024	<4.0	15	13	200
10/15/2024	<4.0	13	17	230
11/12/2024	15	27	95	130
12/09/2024	<4.0	23	33	140
01/12/2025	<4.0	24	30	77
03/10/2025	<4.0	8.9	17	38
04/13/2025	<4.0	17	20	22
05/12/2025	<4.0	27	45	180
06/08/2025	<4.0	18	22	370
07/13/2025	<4.0	13	15	660
08/10/2025	6	18	21	770
09/07/2025	4	8.1	10	650
10/12/2025	<4.0	19	13	650
11/09/2025	4	16	16	550
12/14/2025	4	20	18	540
01/11/2026	<4.1	17	23	190
02/08/2026	4	6.3	11	190
04/13/2026	8.4	16	38	13
05/12/2026	9.6	18	51	72

Notes:

Prepared by: DCF1

1. Blank cells represent an analyte not tested during that event.

Checked by: MAN

2. Significant figures are as reported from the database obtained from White Pine Copper.

mg/L = milligram per liter

µg/L = microgram per liter

Appendix Table I.1-12
Surface Water Quality - Tailings: North Pond #2 - Historical
White Pine Copper LLC

Detected Analytes				
Date	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Chloride (mg/L)
01/08/2006	<4	30	49	
02/12/2006	4	42	56	
03/12/2006	5	50	64	
04/09/2006	10	42	13	
05/07/2006	12	35	11	
06/11/2006	7	43	74	
07/09/2006	<4	29	46	
11/12/2006	24	16	25	
12/10/2006	<4	21	29	
01/14/2007	4	27	37	
02/11/2007	<4	30	36	
03/11/2007	<4	38	42	
04/08/2007	18	60	24	
05/13/2007	16	41	140	
06/10/2007	15	36	80	
10/14/2007	21	21	84	
12/09/2007	<4	44	56	
02/09/2008	<4	60	67	
04/13/2008	6	56	85	
05/11/2008	38	39	200	
02/08/2009	<4	<5.2	20	
03/08/2009	<4	29	33	
04/12/2009	4	42	83	
05/10/2009	25	34	130	
10/11/2009	28	12	90	
11/08/2009	17	31	81	
02/14/2010	<4	41	44	
03/14/2010	<4	46	51	
04/11/2010	17	33	98	
05/09/2010	10	30	58	
10/10/2010	4	11	22	
11/14/2010	<4	18	37	
12/12/2010	<4	25	30	
01/09/2011	<4	62	64	
05/08/2011	12	40	160	
06/12/2011	8	43	67	
07/10/2011	<4	27	47	
11/13/2011	19	21	61	
12/11/2011	11	23	37	

Table I.1-12 (continued)

Detected Analytes				
Date	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Chloride (mg/L)
02/12/2012	<4	35	40	
03/11/2012	<4	49	57	
04/08/2012	28	35	84	
07/08/2012	<4	22	33	
08/12/2012	7	15	41	
09/09/2012	7	5.2	35	
10/14/2012	8	19	30	
11/11/2012	78	39	220	
12/09/2012	<4	37	59	
01/13/2013	<4	48	56	
02/10/2013	<4	57	63	
03/10/2013	<4	45	46	
04/14/2013	<4	36	46	
05/12/2013	44	94	210	
06/09/2013	9	51	84	
07/14/2013	7	27	52	
08/11/2013	15	24	50	
10/13/2013	8	31	51	
11/10/2013	61	30	190	
12/08/2013	<4	64	64	
04/13/2014	4	38	62	
05/11/2014	29	46	240	
06/08/2014	<4	40	56	
08/10/2014	9	16	37	
09/14/2014	10	120	130	
10/12/2014	19	40	120	
11/09/2014	34	43	110	
01/12/2015	<4	39	38	
02/08/2015	4	51	55	
03/08/2015	4	52	60	
04/12/2015	25	42	110	
05/10/2015	23	23	56	
06/14/2015	<4	17	27	
07/12/2015	<4	19	29	
09/13/2015	9	15	38	
10/11/2015	29	18	70	
11/08/2015	27	31	95	
12/13/2015	<4	43	69	
01/10/2016	<4	55	81	100
02/14/2016	<4	33	41	140
03/13/2016	<4	30	33	99
04/10/2016	<4	28	49	51
05/08/2016	10	27	64	130
06/12/2016	4	26	53	150

Table I.1-12 (continued)

Detected Analytes				
Date	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Chloride (mg/L)
06/15/2016	<4	21	32	
07/10/2016	<4	22	32	180
08/14/2016	<4	13	32	
09/11/2016	7	25	59	180
10/09/2016	18	14	45	210
11/13/2016	36	29	150	230
12/11/2016	7	38	60	230
01/08/2017	<4	35	43	270
02/12/2017	<4	54	54	270
03/13/2017	<4	27	48	92
04/09/2017	4	23	44	150
05/08/2017	7	32	73	130
06/11/2017	19	37	88	130
07/09/2017	<4	21	34	150
08/13/2017	<4		27	180
09/10/2017	14	35	89	150
10/08/2017	<4	23	44	210
11/12/2017	<4	35	64	190
12/10/2017	<4	30	57	150
01/08/2018	<4	35	42	190
02/11/2018	<4	32	38	230
03/12/2018	<4	32	39	280
04/08/2018		38	53	320
05/13/2018	6	27	66	120
06/10/2018	10	20	40	160
07/08/2018	16	20	84	190
08/12/2018	<4	15	18	230
09/09/2018	8	15	35	
10/14/2018	15	30	72	
11/11/2018	5	32	65	150
12/09/2018	4	60	58	120
01/13/2019	<4	23	61	130
04/15/2019	4	25	60	54
05/13/2019	16	35	87	81
06/09/2019	4	21	39	100
10/13/2019	11	29	75	220
11/10/2019	<4	27	39	
12/08/2019	14	62	69	110
03/09/2020	<4	32	34	240
04/13/2020	12	22	49	87
05/11/2020	8	25	68	99
06/07/2020	36	23	94	130
07/12/2020	<4	15	25	180
08/09/2020	<4	17	26	180

Table I.1-12 (continued)

Detected Analytes				
Date	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Chloride (mg/L)
09/13/2020	<4	14	26	220
10/11/2020	14	16	31	230
11/08/2020	29	28	71	300
12/13/2020	<4	34	40	320
01/10/2021	<4	39	43	340
03/14/2021	<4	36	45	93
04/12/2021	17	28	74	130
05/10/2021	7	23	48	170
06/14/2021	4	16	19	190
08/08/2021	4	13	19	260
12/12/2021	4	24	33	390
03/14/2022	<4	27	30	750
04/11/2022	11	38	75	42
05/09/2022	40	120	120	75
06/13/2022	4	25	40	70
07/11/2022	4	21	28	71
08/14/2022	5	16	27	87
11/13/2022	12	26	67	110
12/11/2022	<4	33	44	110
01/08/2023	<4	35	35	100
02/12/2023	<4	28	31	130
03/13/2023	<4	30	31	140
04/09/2023	<4	37	40	95
05/08/2023	8.7	76	52	60
06/11/2023	6	11	32	80
12/10/2023	<4	19	26	150
01/14/2024	<4	21	32	190
02/11/2024	<4	25	39	180
03/11/2024	<4	35	33	170
04/15/2024	7	29	42	270
05/13/2024	10	19	46	260
06/09/2024	<4	18	35	270

Notes:

Prepared by: DCF1

Checked by: MAN

1. Sample taken 8/13/2017 for Total Dissolved Solids (530 mg/L) was excluded from the table due to lack of data.

2. Blank cells represent an analyte not tested during that event.

3. Significant figures are as reported from the database obtained from White Pine Copper.

mg/L = milligram per liter

µg/L = microgram per liter

Appendix Table I.1-12a
Surface Water Quality - Tailings: North Pond #2 - (2024-2026)
White Pine Copper LLC

Detected Analytes				
Date	Total Suspended Solids (mg/L)	Dissolved Copper (µg/L)	Total Recoverable Copper (µg/L)	Chloride (mg/L)
07/14/2024	<4.0	27	27	200
09/10/2024	10	17	33	200
10/15/2024	5.1	16	28	220
11/12/2024	32	24	92	180
12/09/2024	<4.0	26	48	170
01/12/2025	<4.0	44	44	56
02/09/2025	<4.0	24	34	85
03/10/2025	<4.0	28	48	74
04/13/2025	<4.0	27	51	28
05/12/2025	11	24	67	74
06/08/2025	<4.0	17	29	91
07/13/2025	<4.0	13	18	110
08/10/2025	<4.0	14	22	140
09/07/2025	8	9.4	32	180
11/09/2025	6.3	16	31	230
12/14/2025	<4.1	31	39	240
01/11/2026	<4.1	56	68	210
02/08/2026	<4.0	25	31	230
03/09/2026	<4.0	62	83	87
04/13/2026	4	18	27	38
05/12/2026	19	22	75	58

Notes:

Prepared by: DCF1

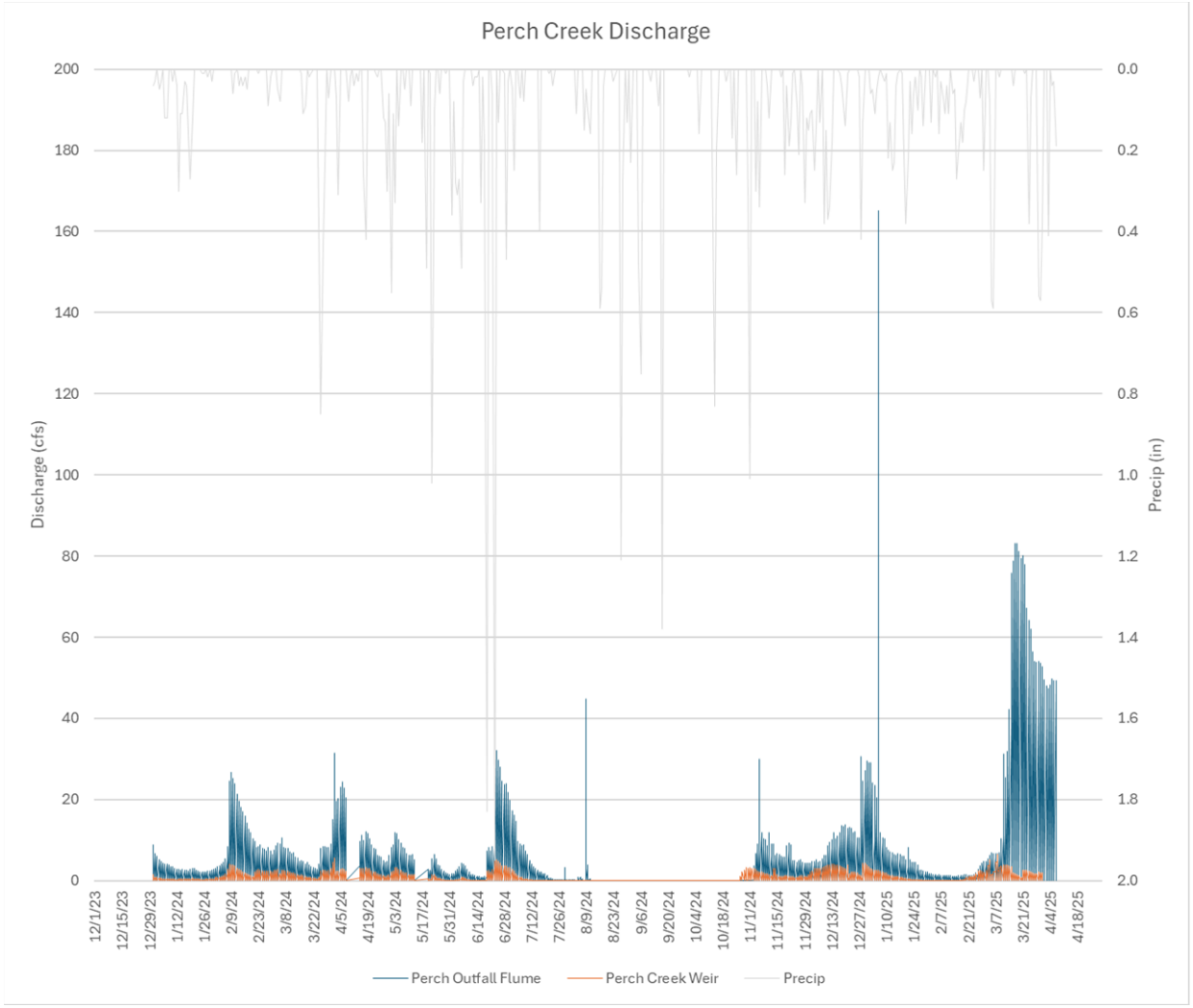
1. Blank cells represent an analyte not tested during that event.

Checked by: MAN

2. Significant figures are as reported from the database obtained from White Pine Copper.

mg/L = milligram per liter

µg/L = microgram per liter



NOTES:

1. Flow recorded automatically every 30 minutes.
2. The flume is the default measuring point; however, when flows drop below 2.2 million gallons per day (4.08 cfs) on the flume record, then the weir record should be substituted (since the flume is less accurate below this threshold).
3. Flow data were not recorded between 4/8/24 - 4/15/24 and 5/13/24 - 5/20/24.
4. Precipitation data from the PRISM Climate Group website (4 km grid).
5. cfs = cubic feet per minute
6. The spike on 8/9/2024 was due to drawdown of an upstream pond. The flume and weir were not functional from mid-August to mid-November 2024.

WHITE PINE COPPER, LLC

FIGURE I.1-1

PERCH CREEK DISCHARGE
GROUNDWATER & SURFACE WATER
BASELINE HYDROLOGY REPORT
WHITE PINE NORTH, ONTONAGON COUNTY, MICHIGAN

Date: AUGUST 2025	Revision Date: JULY 2026	
Drawn By: BJW1	Checked By: MAN	Project: 23W200.00

pw:\White Pine Copper\23W200\10000 Reports\2025 Baseline GW and SW\Appendices\Appendix I - Supplemental Data\I-1 - Supplemental SW Info\Figure I.1-1 (Perch Cr discharge graph)_SW_Updated June 2026.xlsx Date: 8/11/2026

I-2

Supplemental Groundwater Water Quality Information

Appendix Table I.2 - 1
General Summary of Groundwater Analytical Data
White Pine Copper

Constituent and Units	First sample date	Latest sample date	Count of Samples	Count of Results Below Detection Limit	% of Results Below Detection Limit	Average	Minimum Concentration	Maximum Detected Concentration	Standard Deviation
Constituents with >90% of results detected									
Alkalinity (mg/L)	2/18/1994	3/11/2025	313	3	1%	160.4	0	770	148.3
Ammonia-N (N) (CC) (mg/L)	11/29/1994	12/2/1994	6	0	0%	4.98	0.09	28	11.29
Arsenic, Dissolved combined (mg/L)	1/31/1994	3/11/2025	405	24	6%	0.003	0.00017	0.045	0.0014
Arsenic, Total Recoverable combined (mg/L)	11/29/1994	3/11/2025	152	12	8%	0.002	0.00023	0.012	0.0006
Barium, Dissolved combined (mg/L)	1/31/1994	3/11/2025	812	6	1%	0.958	0.002	74	2.45
Barium, Total Recoverable combined (mg/L)	11/29/1994	3/11/2025	442	1	0%	1.01	0.003	73	1.66
Bicarbonate Alkalinity (as CaCO3) (mg/L)	2/18/1994	3/11/2025	341	1	0%	151.9	1	770	144.7
Boron, Dissolved combined (mg/L)	11/29/1994	3/11/2025	615	8	1%	0.729	0.01	7.3	0.376
Boron, Total Recoverable combined (mg/L)	8/23/2006	3/11/2025	414	4	1%	0.760	0.01	7.3	0.324
Calcium, Dissolved combined (mg/L)	6/30/1997	3/11/2025	374	0	0%	151.0	2	24000	368.4
Calcium, Total Recoverable combined (mg/L)	2/18/1994	3/11/2025	172	0	0%	530.1	2.5	24000	521.5
Cation-Anion Balance (%)	6/10/2008	10/16/2024	141	0	0%	-1.07	-10.3	7.1	3.26
Chloride (mg/L)	2/18/1994	3/11/2025	785	5	1%	557.9	0.51	61000	4395
Chlorine (mg/L)	7/15/1997	8/5/1998	13	0	0%	266.5	120	490	114.8
Conductivity Field combined (µS/cm)	2/18/1994	3/11/2025	3519	#N/A	#N/A	714	173	4740	632
Density (g/mL)	11/29/1994	12/2/1994	6	0	0%	1.03	0.998	1.063	0.420
Dissolved Oxygen (Field) (mg/L)	7/9/1997	3/11/2025	202	0	0%	2.58	0	15.83	2.95
Field Iron II, Dissolved (mg/L)	4/13/1998	4/14/1998	11	0	0%	0.654	0	3.3	1.09
Field Iron, Dissolved (mg/L)	4/13/1998	4/14/1998	11	0	0%	0.816	0	4	1.39
Hardness (mg/L)	7/10/2024	3/11/2025	120	0	0%	1053	8.1	60000	5502
HCO3 (mg/L)	7/15/1997	8/5/1998	13	0	0%	238.0	2	500	176.9
Hexavalent Chromium, Dissolved (mg/L)	7/10/2024	7/14/2024	3	0	0%	0.008	0.0064	0.01	0.0020
Iron, Total Recoverable combined (mg/L)	11/29/1994	3/11/2025	442	35	8%	3.89	0.02	123	3.74
Magnesium, Dissolved combined (mg/L)	10/15/1995	3/11/2025	380	9	2%	13.07	0.1	220	7.80
Magnesium, Total Recoverable combined (mg/L)	2/18/1994	3/11/2025	172	0	0%	45.42	0.22	1200	36.22
Manganese, Total Recoverable combined (mg/L)	11/29/1994	3/11/2025	442	27	6%	1.39	0.005	91.2	1.98
pH (Field) (SU)	2/18/1994	3/11/2025	432	#N/A	#N/A	7.95	2.7	11.59	0.867
pH (Lab) (SU)	2/18/1994	8/11/2016	151	#N/A	#N/A	7.88	6.3	9.95	0.704
Potassium, Dissolved combined (mg/L)	2/18/1994	3/11/2025	308	0	0%	5.73	0.22	109	3.83
Potassium, Total Recoverable combined(mg/L)	7/20/1999	3/11/2025	142	0	0%	4.43	0.25	44	1.39
Pyrene (µg/L)	10/26/2015	10/28/2015	6	0	0%	0.830	0.83	0.83	0.00
Radon-222 (pCi/L)	9/29/2009	9/29/2009	1	0	0%	110.0	110	110	#DIV/0!
Redox Potential (Field) (mV)	7/9/1997	3/11/2025	182	0	0%	117.0	-273	598	191.4
Residue, Filterable (TDS) at 180'C (mg/L)	8/10/1998	10/16/2024	229	0	0%	280.9	118	1770	273.9
Silicone, Dissolved (mg/L)	2/18/1994	12/2/1994	17	0	0%	10.11	5.5	19.2	4.30
Silicone, Total Recoverable (mg/L)	11/29/1994	12/2/1994	6	0	0%	15.10	6.5	39	12.58
Sodium, Dissolved combined (mg/L)	2/18/1994	3/11/2025	406	0	0%	218.4	6.4	11000	290.3
Sodium, Total Recoverable combined (mg/L)	7/15/1997	3/11/2025	155	0	0%	274.9	6.4	8500	154.0
Strontium, Dissolved combined(mg/L)	1/31/1994	3/11/2025	820	0	0%	5.93	0.01	940	21.77
Strontium, Total Recoverable combined(mg/L)	11/29/1994	3/11/2025	442	0	0%	4.17	0.02	410	8.62
Sulfate (mg/L)	2/18/1994	3/11/2025	406	22	5%	31.65	0.21	640	52.31
Sum of Anions (meq/L)	6/10/2008	10/16/2024	141	0	0%	2.68	2.1	3.5	0.215
Sum of Cations (meq/L)	6/10/2008	10/16/2024	141	0	0%	2.62	2.3	3.8	0.200
TDS (calculated) (mg/L)	6/10/2008	10/16/2024	141	0	0%	156.8	129	244	15.11
Total Dissolved Solids combined (mg/L)	2/18/1994	3/11/2025	289	#N/A	#N/A	2479	129	102000	3158
TDS (ratio - measured/calculated)	6/10/2008	10/16/2024	141	0	0%	1.04	0.84	1.66	0.127
Temperature Lab (°C)	2/18/1994	8/11/2016	147	#N/A	#N/A	15.61	6	25.4	5.34
Temperature combined (°C)	2/18/1994	3/11/2025	561	#N/A	#N/A	11.98	3.58	26.73	4.30
Total Alkalinity as CaCO3 at pH 4.5 (mg/L)	8/10/1998	8/17/2000	25	0	0%	110.7	72	174	23.87
Turbidity (NTU)	7/24/2024	3/11/2025	105	0	0%	43.77	0	278	61.42
Uranium, Dissolved (µg/L)	7/10/2024	3/11/2025	117	5	4%	8.24	0.010	72	14.83
Uranium, Total Recoverable (µg/L)	7/10/2024	3/11/2025	119	2	2%	8.32	0.010	74	14.82
Constituents with >10%, but <50% of results less than Reporting Limit									
Acidity (g/mL)	11/29/1994	12/2/1994	6	2	33%	39.00	2	135	51.3
Aluminum, Total Recoverable combined (mg/L)	11/29/1994	3/11/2025	126	42	33%	1.212	0.025	19	0.582
Bromide (mg/L)	2/18/1994	3/11/2025	137	38	28%	22.36	0.1	830	95.8
Carbon, Dissolved Organic (mg/L)	8/14/2013	3/11/2025	156	23	15%	2.66	0.47	9.7	2.06
Chromium III, Total (mg/L)	7/10/2024	7/14/2024	3	1	33%	0.014	0.01	0.022	0.0069
Chromium, Total Recoverable combined (mg/L)	1/31/1994	3/11/2025	234	102	44%	0.013	0.0005	0.25	0.0054
Copper, Total Recoverable combined (mg/L)	11/29/1994	3/11/2025	159	27	17%	0.075	0.0005	2.66	0.062
Fluoride (mg/L)	2/18/1994	3/11/2025	240	44	18%	0.788	0	10	1.15
Hexavalent Chromium, Total (mg/L)	7/10/2024	7/14/2024	3	1	33%	0.0064	0.0032	0.01	0.0034
Hydrocarbons (mg/L)	2/18/1994	10/15/1998	107	12	11%	245.5	0.1	820	196.3
Lithium, Dissolved combined (mg/L)	11/29/1994	3/11/2025	628	143	23%	0.066	0.0025	3.6	0.096
Lithium, Total Recoverable combined (mg/L)	11/29/1994	3/11/2025	420	96	23%	0.073	0.0025	3.15	0.082
Manganese, Dissolved combined (mg/L)	1/31/1994	3/11/2025	829	232	28%	0.604	0.00079	25.9	0.895
Mercury, Dissolved combined (ng/L)	1/31/1994	3/11/2025	242	59	24%	12460	0.2	2000100	33713
Mercury, Total Recoverable combined (ng/L)	11/29/1994	3/11/2025	132	32	24%	16.49	0.2	200	9.01
Molybdenum, Dissolved combined (mg/L)	11/29/1994	3/11/2025	240	39	16%	0.017	0.001	0.17	0.0064
Molybdenum, Total Recoverable combined (mg/L)	11/29/1994	3/11/2025	126	37	29%	0.019	0.001	0.17	0.0055
Nickel, Total Recoverable combined (mg/L)	11/29/1994	3/11/2025	156	75	48%	0.0053	0.00063	0.1	0.0022
Nitrate/Nitrite as N (N) (mg/L)	2/18/1994	3/11/2025	301	137	46%	0.287	0.01	19	1.21
Kjeldahl Nitrogen, Total Recoverable (mg/L)	2/18/1994	12/2/1994	17	7	41%	1.05	0.1	6.03	1.50
Phenol combined (mg/L)	7/20/1999	10/16/2024	171	80	47%	0.013	0.00041	0.28	0.0067
Phosphorus-Total (as P) (mg/L)	7/10/2024	3/11/2025	125	58	46%	0.092	0.024	0.79	0.127
Total Organic Carbon (TOC) (mg/L)	7/20/1999	3/11/2025	284	33	12%	2.84	0.47	17	2.62
Total Suspended Solids (mg/L)	11/29/1994	3/11/2025	213	26	12%	237.0	1.9	2100	378.8
Vanadium, Total Recoverable combined(µg/L)	11/29/1994	3/11/2025	148	74	50%	6.11	0.0000025	97	2.41

Appendix Table I.2 - 1
General Summary of Groundwater Analytical Data
White Pine Copper

Constituent and Units	First sample date	Latest sample date	Count of Samples	Count of Results Below Detection Limit	% of Results Below Detection Limit	Average	Minimum Concentration	Maximum Detected Concentration	Standard Deviation
Constituents with >50%, but <100% of results less than Reporting Limit									
1,2-Dichlorobenzene (VOC) (µg/L)	6/10/2008	10/16/2024	147	143	97%	0.488	0.2	0.5	0.060
2-Butanone (µg/L)	6/10/2008	10/16/2024	147	141	96%	0.630	0.5	6.6	0.626
2-Hexanone (µg/L)	6/10/2008	10/16/2024	147	146	99%	0.500	0.5	0.5	0.000
Acetone (µg/L)	6/10/2008	10/16/2024	147	137	93%	1.759	0.5	2.5	0.521
Acrylonitrile (µg/L)	6/10/2008	10/16/2024	147	145	99%	0.418	0.05	2	0.574
Aluminum, Dissolved combined (mg/L)	2/1/1994	3/11/2025	138	112	81%	0.160	0.025	6.2	0.129
Ammonia (mg/L)	7/10/2024	3/11/2025	118	91	77%	0.185	0.1	1.7	0.255
Antimony, Dissolved (mg/L)	11/29/1994	10/16/2024	180	142	79%	0.001	0.0004	0.042	0.004
Antimony, Total Recoverable combined (mg/L)	11/29/1994	3/11/2025	148	146	99%	0.001	0.001	0.01	0.000
Benzene (µg/L)	6/10/2008	10/16/2024	147	145	99%	0.306	0.2	0.7	0.147
Beryllium, Total Recoverable combined(mg/L)	7/20/1999	3/11/2025	142	130	92%	0.001	0.00025	0.003	0.000
Bis(2-ethylhexyl)phthalate (µg/L)	10/26/2015	10/28/2015	6	4	67%	0.900	0.72	1.6	0.352
Cadmium, Dissolved combined (mg/L)	1/31/1994	3/11/2025	434	307	71%	0.001	0.000037	0.15	0.003
Cadmium, Total Recoverable combined (mg/L)	11/29/1994	3/11/2025	148	137	93%	0.000	0.0001	0.0061	0.000
Carbonate Alkalinity (as CaCO3) (mg/L)	8/10/1998	3/11/2025	324	174	54%	9.393	1	162	16.363
Chemical Oxygen Demand (mg/L)	7/20/1999	10/16/2024	165	87	53%	20.048	5	150	22.225
Chromium III, Dissolved (mg/L)	7/10/2024	7/14/2024	3	2	67%	0.010	0.01	0.01	0.000
Chromium, Dissolved combined (mg/L)	1/31/1994	3/11/2025	376	288	77%	0.011	0.0005	0.25	0.005
Cobalt, Dissolved combined (mg/L)	11/29/1994	3/11/2025	288	258	90%	0.007	0.0004	0.02	0.002
Cobalt, Total Recoverable combined(mg/L)	11/29/1994	3/11/2025	148	93	63%	0.002	0.0004	0.025	0.001
Copper, Dissolved combined (mg/L)	1/31/1994	3/11/2025	414	241	58%	0.009	0.0005	0.5	0.008
Cyanide, Total (mg/L)	7/20/1999	3/11/2025	285	274	96%	0.005	0.003	0.13	0.009
Ethylbenzene (µg/L)	6/10/2008	10/16/2024	147	146	99%	0.307	0.2	0.9	0.151
Iron, Dissolved combined (mg/L)	2/1/1994	3/11/2025	762	402	53%	0.592	0.01	36	0.898
Lead, Dissolved combined (mg/L)	1/31/1994	3/11/2025	424	282	67%	0.006	0.0001	0.5	0.011
Lead, Total Recoverable combined (mg/L)	11/29/1994	3/11/2025	148	92	62%	0.002	0.00019	0.085	0.001
m&p-xylene (µg/L)	6/10/2008	10/16/2024	147	145	99%	0.443	0.4	0.8	0.064
Methyl Mercury, Dissolved (ng/L)	7/10/2024	3/11/2025	118	109	92%	0.030	0.022	0.82	0.074
Methyl Mercury, Total Recoverable (ng/L)	7/10/2024	3/11/2025	118	101	86%	0.029	0.022	0.35	0.038
Methylene chloride (µg/L)	6/10/2008	10/16/2024	147	143	97%	0.555	0.3	4.5	0.434
Nickel, Dissolved combined (mg/L)	2/1/1994	3/11/2025	374	247	66%	0.014	0.00063	0.5	0.013
Nitrate as N (mg/L)	7/10/2024	3/11/2025	121	92	76%	0.485	0.043	8.6	1.082
Nitrite as N (mg/L)	7/10/2024	3/11/2025	120	117	98%	0.238	0.07	10	0.907
Nitrogen, ammonia (N) (CC) (mg/L)	7/20/1999	10/16/2024	165	126	76%	0.078	0.025	0.81	0.087
Salinity (PSU)	7/10/2024	3/11/2025	120	65	54%	2.352	0.33	110	10.278
Selenium, Dissolved combined (mg/L)	1/31/1994	3/11/2025	431	278	65%	0.002	0.0001	0.038	0.001
Selenium, Total Recoverable combined (mg/L)	11/29/1994	3/11/2025	148	126	85%	0.001	0.0005	0.0023	0.000
Silver, Dissolved combined (mg/L)	1/31/1994	3/11/2025	404	306	76%	0.001	0.00005	0.25	0.004
Silver, Total Recoverable combined (mg/L)	11/29/1994	3/11/2025	148	141	95%	0.001	0.00012	0.015	0.000
Sulfide (mg/L)	7/10/2024	3/11/2025	118	96	81%	0.617	0.23	8.7	1.231
Thallium, Dissolved combined (mg/L)	11/29/1994	3/11/2025	296	284	96%	0.071	0.0001	10	0.213
Tin, Dissolved (µg/L)	7/10/2024	3/11/2025	117	113	97%	1.415	1.3	5	0.616
Tin, Total Recoverable (µg/L)	7/10/2024	3/11/2025	120	104	87%	1.513	1.3	5	0.684
Toluene (µg/L)	6/10/2008	10/16/2024	147	143	97%	0.322	0.2	1.6	0.205
Vanadium, Dissolved combined (mg/L)	11/29/1994	3/11/2025	296	212	72%	0.008	0.0022	0.3	0.007
Zinc, Dissolved combined (mg/L)	1/31/1994	3/11/2025	404	253	63%	0.087	0.0045	23	0.348
Zinc, Total Recoverable combined (mg/L)	11/29/1994	3/11/2025	148	79	53%	0.217	0.005	21	0.321
Constituents with 100% of results less than Reporting Limit									
1,1,1,2-Tetrachloroethane (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
1,1,1-Trichloroethane (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
1,1,2,2-Tetrachloroethane (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.24442	0.01	0.5	0.2408
1,1,2-Trichloroethane (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
1,1`-Biphenyl (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.63000	0.63	0.63	0.0000
1,1-Dichloroethane (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.49184	0.3	0.5	0.0397
1,1-Dichloroethene (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.49184	0.3	0.5	0.0397
1,1-Dichloropropene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.20000	0.2	0.2	0.0000
1,2,3-Trichlorobenzene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.20000	0.2	0.2	0.0000
1,2,3-Trichloropropane (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
1,2,4-Trichlorobenzene (VOC) (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.20000	0.2	0.2	0.0000
1,2,4-Trimethylbenzene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.20000	0.2	0.2	0.0000
1,2-Dibromo-3-chloropropane (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.49184	0.3	0.5	0.0397
1,2-Dibromoethane (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.24442	0.01	0.5	0.2408
1,2-Dichloroethane (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
1,2-Dichloropropane (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.49184	0.3	0.5	0.0397
1,3,5-Trimethylbenzene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.20000	0.2	0.2	0.0000
1,3-Dichlorobenzene (VOC) (µg/L)	5/26/2009	10/16/2024	135	135	100%	0.48667	0.2	0.5	0.0621
1,3-Dichloropropane (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.20000	0.2	0.2	0.0000
1,4-Dichlorobenzene (VOC) (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
2,2`-oxybis[1-chloropropane] (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.93000	0.93	0.93	0.0000
2,2-Dichloropropane (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.20000	0.2	0.2	0.0000
2,4,5-T (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.14000	0.14	0.14	0.0000
2,4,5-Trichlorophenol (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.49000	0.49	0.49	0.0000
2,4,6-Trichlorophenol (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.53000	0.53	0.53	0.0000
2,4-D (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.16000	0.16	0.16	0.0000
2,4-Dichlorophenol (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.63000	0.63	0.63	0.0000
2,4-Dimethylphenol (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.91000	0.91	0.91	0.0000
2,4-Dinitrophenol (µg/L)	10/26/2015	10/28/2015	6	6	100%	2.40000	2.4	2.4	0.0000
2,4-Dinitrotoluene (µg/L)	10/26/2015	10/28/2015	6	6	100%	1.00000	1	1	0.0000
2,6-Dinitrotoluene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.88000	0.88	0.88	0.0000
2-Chloroethyl vinyl ether (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.50000	0.5	0.5	0.0000
2-Chloronaphthalene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.61000	0.61	0.61	0.0000
2-Chlorophenol (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.74000	0.74	0.74	0.0000

Appendix Table I.2 - 1
General Summary of Groundwater Analytical Data
White Pine Copper

Constituent and Units	First sample date	Latest sample date	Count of Samples	Count of Results Below Detection Limit	% of Results Below Detection Limit	Average	Minimum Concentration	Maximum Detected Concentration	Standard Deviation
2-Chlorotoluene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.20000	0.2	0.2	0.0000
2-Methyl-4,6-dinitrophenol (µg/L)	10/26/2015	10/28/2015	6	6	100%	2.00000	2	2	0.0000
2-Methylnaphthalene (SVOC) (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.88000	0.88	0.88	0.0000
2-Methylnaphthalene (VOC) (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.20000	0.2	0.2	0.0000
2-Methylphenol (µg/L)	10/26/2015	10/28/2015	6	6	100%	1.30000	1.3	1.3	0.0000
2-Nitroaniline (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.65000	0.65	0.65	0.0000
2-Nitrophenol (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.59000	0.59	0.59	0.0000
3,3-Dichlorobenzidine (µg/L)	10/26/2015	10/28/2015	6	6	100%	1.00000	1	1	0.0000
3-Nitroaniline (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.82000	0.82	0.82	0.0000
4,4`-DDD (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.00502	0.005	0.0051	0.0000
4,4`-DDE (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.00402	0.004	0.0041	0.0000
4,4`-DDT (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.00402	0.004	0.0041	0.0000
4-Bromophenylphenyl Ether (µg/L)	10/26/2015	10/28/2015	6	6	100%	1.00000	1	1	0.0000
4-Chloro-3-methylphenol (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.76000	0.76	0.76	0.0000
4-Chloroaniline (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.73000	0.73	0.73	0.0000
4-Chlorophenylphenyl Ether (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.96000	0.96	0.96	0.0000
4-Chlorotoluene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.20000	0.2	0.2	0.0000
4-Methyl-2-pentanone (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.49184	0.3	0.5	0.0397
4-Methylphenol (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.87000	0.87	0.87	0.0000
4-Nitroaniline (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.48000	0.48	0.48	0.0000
4-Nitrophenol (µg/L)	10/26/2015	10/28/2015	6	6	100%	4.70000	4.7	4.7	0.0000
Acenaphthene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.88000	0.88	0.88	0.0000
Acenaphthylene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.65000	0.65	0.65	0.0000
Acetophenone (µg/L)	10/26/2015	10/28/2015	6	6	100%	1.00000	1	1	0.0000
Acrolein (µg/L)	10/26/2015	10/28/2015	6	6	100%	1.30000	1.3	1.3	0.0000
Aldrin (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.00402	0.004	0.0041	0.0000
alpha-BHC (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.00602	0.006	0.0061	0.0000
Anthracene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.57000	0.57	0.57	0.0000
Aroclor-1016 (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.09800	0.098	0.098	0.0000
Aroclor-1221 (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.09800	0.098	0.098	0.0000
Aroclor-1232 (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.09800	0.098	0.098	0.0000
Aroclor-1242 (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.09800	0.098	0.098	0.0000
Aroclor-1248 (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.09800	0.098	0.098	0.0000
Aroclor-1254 (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.08400	0.084	0.084	0.0000
Aroclor-1260 (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.08400	0.084	0.084	0.0000
Atrazine (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.77000	0.77	0.77	0.0000
Benzaldehyde (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.86000	0.86	0.86	0.0000
Benzo(a)anthracene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.55000	0.55	0.55	0.0000
Benzo(a)pyrene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.16000	0.16	0.16	0.0000
Benzo(b)fluoranthene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.44000	0.44	0.44	0.0000
Benzo(g,h,i)perylene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.75000	0.75	0.75	0.0000
Benzo(k)fluoranthene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.18000	0.18	0.18	0.0000
Beryllium, Dissolved Combined (mg/L)	7/20/1999	3/11/2025	282	281	100%	0.00028	0.00005	0.00053	0.0001
beta-BHC (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.00502	0.005	0.0051	0.0000
Bis(2-chloroethoxy)methane (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.69000	0.69	0.69	0.0000
Bis(2-chloroethyl)ether (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.12000	0.12	0.12	0.0000
Bromobenzene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.20000	0.2	0.2	0.0000
Bromochloromethane (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
Bromodichloromethane (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
Bromoform (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
Bromomethane (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.56122	0.5	2	0.2978
Butyl Benzyl Phthalate (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.60000	0.6	0.6	0.0000
Caprolactam (µg/L)	10/26/2015	10/28/2015	6	6	100%	1.10000	1.1	1.1	0.0000
Carbazole (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.85000	0.85	0.85	0.0000
Carbon disulfide (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.50000	0.5	0.5	0.0000
Carbon tetrachloride (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.49184	0.3	0.5	0.0397
Chlordane (technical) (J) (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.13000	0.13	0.13	0.0000
Chlorobenzene (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
Chloroethane (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
Chloroform (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
Chloromethane (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
Chrysene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.67000	0.67	0.67	0.0000
Cis-1,2-Dichloroethene (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
Cis-1,3-Dichloropropene (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
delta-BHC (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.00602	0.006	0.0061	0.0000
Dibenzo(a,h)anthracene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.09000	0.09	0.09	0.0000
Dibenzofuran (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.85000	0.85	0.85	0.0000
Dibromochloromethane (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
Dibromomethane (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.24442	0.01	0.5	0.2408
Dichlorodifluoromethane (µg/L)	5/26/2009	10/16/2024	135	135	100%	0.49111	0.3	0.5	0.0414
Dieldrin (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.00402	0.004	0.0041	0.0000
Diethyl Ether (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.20000	0.2	0.2	0.0000
Diethyl Phthalate (µg/L)	10/26/2015	10/28/2015	6	6	100%	1.00000	1	1	0.0000
Dimethyl Phthalate (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.98000	0.98	0.98	0.0000
Di-N-Butyl Phthalate (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.82000	0.82	0.82	0.0000
Di-N-Octyl Phthalate (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.69000	0.69	0.69	0.0000
Endosulfan I (J) (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.00502	0.005	0.0051	0.0000
Endosulfan II (J) (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.00402	0.004	0.0041	0.0000
Endosulfan sulfate (J) (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.00502	0.005	0.0051	0.0000
Endrin (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.00402	0.004	0.0041	0.0000
Endrin aldehyde (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.00402	0.004	0.0041	0.0000
Endrin ketone (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.00402	0.004	0.0041	0.0000
Fluoranthene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.72000	0.72	0.72	0.0000
Fluorene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.80000	0.8	0.8	0.0000
gamma-BHC (Lindane) (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.00402	0.004	0.0041	0.0000
Heptachlor (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.00402	0.004	0.0041	0.0000
Heptachlor epoxide (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.00402	0.004	0.0041	0.0000

Appendix Table I.2 - 1
General Summary of Groundwater Analytical Data
White Pine Copper

Constituent and Units	First sample date	Latest sample date	Count of Samples	Count of Results Below Detection Limit	% of Results Below Detection Limit	Average	Minimum Concentration	Maximum Detected Concentration	Standard Deviation
Hexachlorobenzene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.47000	0.47	0.47	0.0000
Hexachlorobutadiene (VOC) (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.20000	0.2	0.2	0.0000
Hexachlorocyclopentadiene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.61000	0.61	0.61	0.0000
Hexachloroethane (SVOC) (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.09000	0.09	0.09	0.0000
Hexachloroethane (VOC) (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.30000	0.3	0.3	0.0000
Hydroxide as CaCO3 (mg/L)	8/10/1998	10/16/2024	204	203	100%	1.93137	1	12	0.7785
Indeno(1,2,3-c,d)pyrene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.21000	0.21	0.21	0.0000
Iodomethane (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.52041	0.5	1	0.0993
Isophorone (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.67000	0.67	0.67	0.0000
Isopropylbenzene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.20000	0.2	0.2	0.0000
Mercury, Low Level (ng/L)	9/30/2024	9/30/2024	2	2	100%	0.50000	0.5	0.5	0.0000
Methoxychlor (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.00402	0.004	0.0041	0.0000
Methyl tert-butyl ether (MTBE) (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.20000	0.2	0.2	0.0000
Naphthalene (SVOC) (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.80000	0.8	0.8	0.0000
Naphthalene (VOC) (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.20000	0.2	0.2	0.0000
n-Butylbenzene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.20000	0.2	0.2	0.0000
Nitrobenzene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.49000	0.49	0.49	0.0000
N-Nitrosodi-N-Propylamine (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.83000	0.83	0.83	0.0000
N-Nitrosodiphenylamine (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.74000	0.74	0.74	0.0000
n-Propylbenzene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.20000	0.2	0.2	0.0000
o-Xylene (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.30408	0.2	0.5	0.1433
Pentachlorophenol (µg/L)	10/26/2015	10/28/2015	6	6	100%	2.20000	2.2	2.2	0.0000
Phenanthrene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.65000	0.65	0.65	0.0000
Phenol (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.41000	0.41	0.41	0.0000
p-Isopropyltoluene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.20000	0.2	0.2	0.0000
sec-Butylbenzene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.30000	0.3	0.3	0.0000
Silvex (2,4,5-TP) (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.13000	0.13	0.13	0.0000
Styrene (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
tert-Butylbenzene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.30000	0.3	0.3	0.0000
Tetrachloroethene (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
Thallium, Total Recoverable combined (mg/L)	11/29/1994	3/11/2025	148	148	100%	0.02097	0.00057	2	0.0309
Toxaphene (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.06017	0.06	0.061	0.0004
trans-1,2-Dichloroethene (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
trans-1,3-Dichloropropene (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
trans-1,4-Dichloro-2-butene (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.54626	0.3	2.5	0.3303
Trichloroethene (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
Trichlorofluoromethane (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.48776	0.2	0.5	0.0596
Vinyl acetate (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.49184	0.3	0.5	0.0397
Vinyl chloride (µg/L)	6/10/2008	10/16/2024	147	147	100%	0.25347	0.02	0.5	0.2359
Xylenes, Total (µg/L)	10/26/2015	10/28/2015	6	6	100%	0.70000	0.7	0.7	0.0000

Prepared By: MJG4
Checked by: GMB

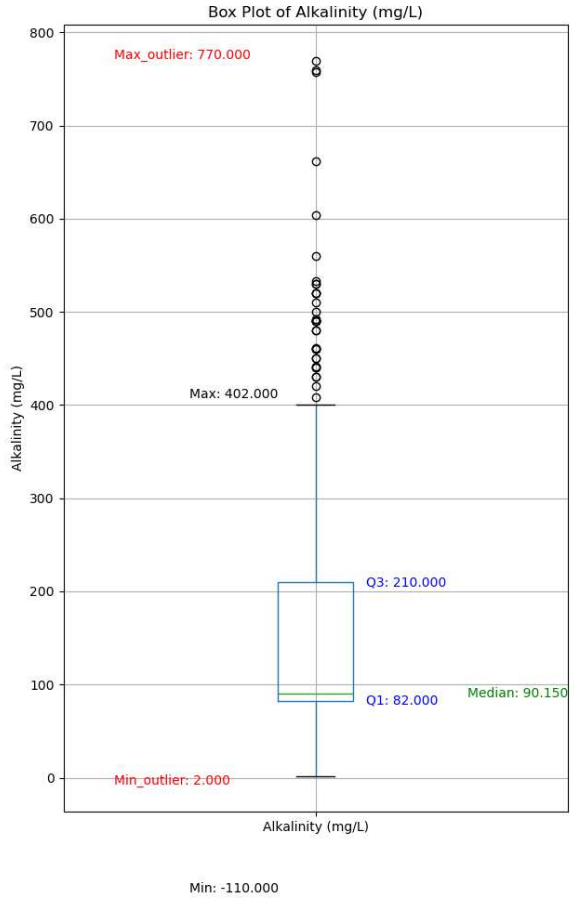
Notes:
Constituents listed as "combined" account for results that underwent conversions so units were consistent for all concentrations.
µg/L = micrograms per liter
µS/cm = microsiemens per centimeter
mg/L = milligrams per liter
ng/L = nanograms per liter
PSU = Practical Salinity Unit
SU = standard units
TDS = total dissolved solids
VOC = Volatile organic compound

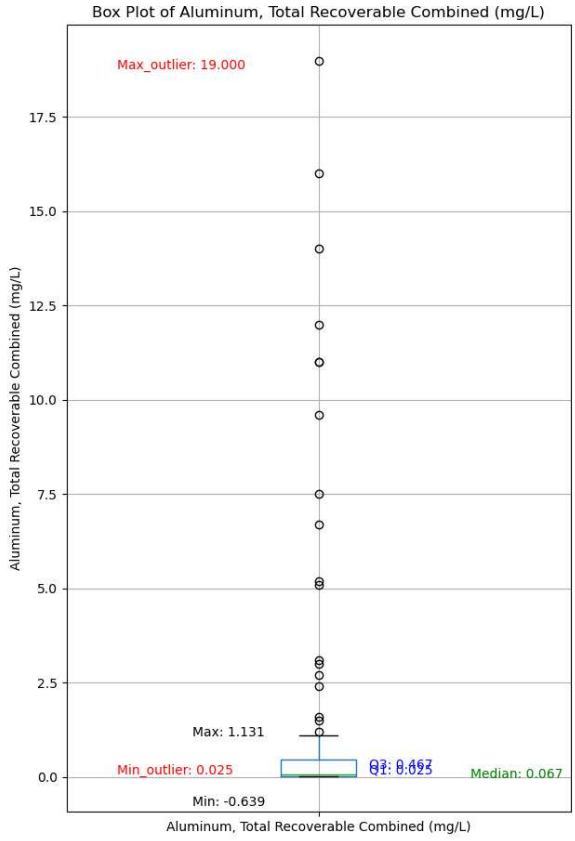
Appendix Table I.2-2
Summary of Supplemental Groundwater Dataset used for Box Plots
(constituents with a minimum of 10 samples)

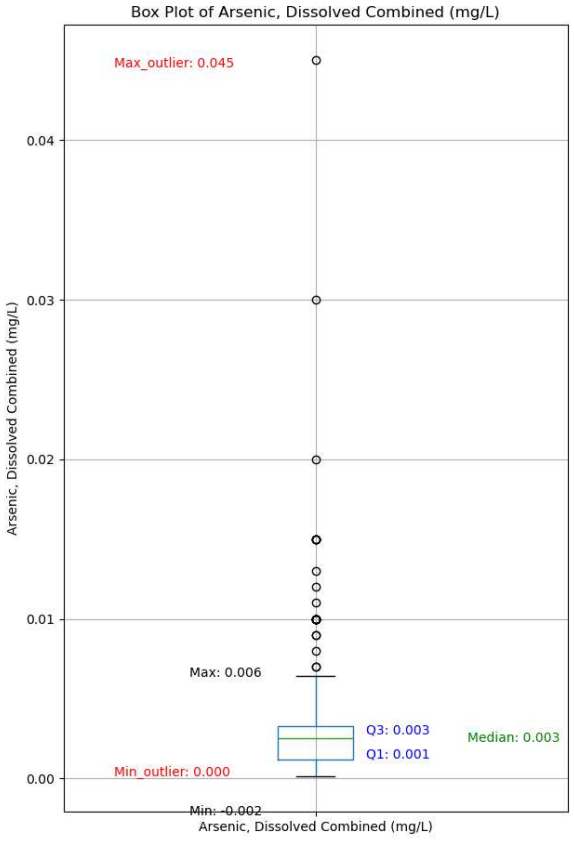
Constituent and Units	Count of Samples	Average	Standard Deviation	Minimum Concentration	Maximum Detected Concentration	First Quartile (Q1) Concentration	Median Concentration	Third Quartile (Q3) Concentration	Interquartile Range	Lower Whisker Concentration	Upper Whisker Concentration	Minimum Outlier	Maximum Outlier	Number of Outliers
Alkalinity (mg/L)	304	165.2	147.88	2	770	82	90.15	210	128	0.0	402	408	770	35
Aluminum, Total Recoverable combined (mg/L)	126	1.21	3.2375	0.025	19	0.025	0.067	0.4675	0.442	0.0	1.131	1.2	19	18
Arsenic, Dissolved combined (mg/L)	405	0.0031	0.0036	0.00017	0.045	0.0012	0.0025	0.0033	0.0021	0.0	0.00645	0.007	0.045	28
Arsenic, Total Recoverable combined (mg/L)	150	0.0022	0.0024	0.00023	0.012	0.0006	0.00115	0.00265	0.0021	0.0	0.0058	0.006	0.012	15
Barium, Dissolved combined (mg/L)	812	0.958	5.6484	0.002	74	0.0409	0.1085	0.45	0.4091	0.0	1.0636	1.08	74	86
Barium, Total Recoverable combined (mg/L)	442	1.01	5.1539	0.003	73	0.087	0.2345	0.61825	0.5313	0.0	1.4151	1.5	73	52
Boron, Dissolved combined (mg/L)	615	0.729	0.7434	0.01	7.3	0.18	0.56	1.145	0.965	0.0	2.5925	2.7	7.3	10
Boron, Total Recoverable combined (mg/L)	414	0.760	0.7697	0.01	7.3	0.21	0.5755	1.2	0.99	0.0	2.685	2.7	7.3	5
Bromide (mg/L)	137	22.36	95.84	0.1	830	0.45	1	4.6	4.15	0.0	10.83	11	830	23
Calcium, Dissolved combined (mg/L)	372	151.0	1260.04	2	24000	8.9	12	80.6	71.725	0.0	188.2	207	24000	43
Calcium, Total Recoverable combined (mg/L)	172	530.1	2592.8	2.5	24000	19	63	160	141	0.0	371.5	380	24000	18
Carbon, Dissolved Organic (mg/L)	156	2.66	2.0644	0.47	9.7	1	2.2	3.7	2.7	0.0	7.75	7.8	9.7	3
Cation-Anion Balance (%)	101	-1.4960	3.7786	-10.3	7.1	-3.8	-2	1.9	5.7	0.0	10.45	---	---	0
Chloride (mg/L)	785	557.9	4394.5	0.51	61000	6	41	160	154	0.0	391	400	61000	67
Chlorine (mg/L)	13	266.5	114.84	120	490	200	240	260	60	110	350	385	490	3
Chromium, Total Recoverable combined (mg/L)	234	0.013	0.0200	0.0005	0.25	0.0011	0.005	0.025	0.0239	0.0	0.0609	0.07	0.25	3
Conductivity Field combined (µS/cm)	500	226602.2	525559.9	173	2870000	320	735	22365	22045	0.0	55432.5	109440	2870000	121
Copper, Dissolved (mg/L)	123	2.70	8.94	0.5	70	0.5	0.54	1.35	0.85	0.0	2.625	2.9	70	20
Copper, Total Recoverable combined (mg/L)	159	0.075	0.3164	0.0005	2.66	0.00125	0.0031	0.011	0.00975	0.0	0.0256	0.027	2.66	25
Fluoride (mg/L)	236	0.802	1.1594	0.1	10	0.3	0.485	0.8925	0.5925	0.0	1.7813	1.8	10	17
Hardness (mg/L)	120	1052.8	5502.5	8.1	60000	92.75	225	642.5	549.75	0.0	1467.13	2400	60000	9
HCO3- (Bicarbonate) (mg/L)	354	155.1	146.60	1	770	68.2	85.05	200	131.775	0.0	397.7	400	770	40
Hydrocarbons (mg/L)	107	245.5	196.32	0.1	820	100	202	400	300	0.0	850	---	---	0
Iron, Dissolved (mg/L)	123	665.5	1292.2	47	7900	47	54	685	638	0.0	1642	1700	7900	17
Iron, Total Recoverable combined (mg/L)	442	3.89	11.22	0.02	123	0.12	0.795	2.6	2.48	0.0	6.32	6.46	123	63
Lead, Total Recoverable (mg/L)	28	0.0035	0.0038	0.0005	0.018	0.001	0.0025	0.005	0.004	0.0	0.011	0.018	0.018	1
Lithium, Dissolved combined (mg/L)	628	0.066	0.2477	0.0025	3.6	0.02	0.03	0.05225	0.032	0.0	0.101	0.101	3.6	39
Lithium, Total Recoverable combined (mg/L)	420	0.073	0.2549	0.0025	3.15	0.02	0.0314	0.06	0.04	0.0	0.12	0.13	3.15	26
Magnesium, Dissolved combined (mg/L)	380	13.07	23.44	0.1	220	1.1	1.75	12.25	11.15	0.0	28.98	30	220	56
Magnesium, Total Recoverable combined (mg/L)	172	45.42	178.19	0.22	1200	2.7	8.65	15.25	12.55	0.0	34.08	35	1200	35
Manganese, Dissolved combined (mg/L)	829	0.604	1.9901	0.00079	25.9	0.008	0.04	0.381	0.373	0.0	0.9405	0.954	25.9	130
Manganese, Total Recoverable combined (mg/L)	442	1.39	6.1062	0.005	91.2	0.05025	0.2	0.93825	0.888	0.0	2.270	2.3	91.2	46
Mercury, Dissolved combined (ng/L)	240	63.43	68.31	0.2	260	0.34	100	100	99.66	0.0	249.49	260	260	1
Mercury, Total Recoverable (ng/L)	120	1.13	2.0733	0.2	19	0.2775	0.5	1	0.722	0.0	2.084	2.4	19	17
Mercury, Total Recoverable combined (ng/L)	132	16.49	49.61	0.2	200	0.3175	0.57	1.675	1.358	0.0	3.71	3.9	200	18
Molybdenum, Dissolved combined (mg/L)	240	0.017	0.0218	0.001	0.17	0.005	0.01	0.02	0.015	0.0	0.0425	0.0457	0.17	24
Molybdenum, Total Recoverable combined (mg/L)	126	0.019	0.0266	0.001	0.17	0.0025	0.00785	0.024	0.0215	0.0	0.0563	0.066	0.17	8
Nickel, Total Recoverable combined (mg/L)	156	0.0053	0.0106	0.00063	0.1	0.00063	0.001	0.005	0.0044	0.0	0.0116	0.012	0.1	18
Nitrate/Nitrite as N (N) (mg/L)	301	0.287	1.2109	0.01	19	0.04	0.07	0.18	0.14	0.0	0.39	0.42	19	30
Kjeldahl Nitrogen, Total Recoverable (mg/L)	17	1.05	1.4983	0.1	6.03	0.1	0.63	0.96	0.86	0.0	2.25	2.6	6.03	2
pH (Field) (SU)	432	7.95	0.87	2.7	11.59	7.33	7.9	8.5425	1.2125	5.5	10.36	2.7	11.59	2
pH (Lab) (SU)	151	7.88	0.70	6.3	9.95	7.4	7.9	8.3	0.9	6.1	9.65	9.95	9.95	2
Phenol combined (mg/L)	169	0.013	0.0318	0.00041	0.28	0.003	0.007	0.007	0.004	0.0	0.013	0.0137	0.28	20
Phosphorus-Total (as P) (mg/L)	125	0.092	0.1265	0.024	0.79	0.024	0.028	0.12	0.096	0.0	0.264	0.27	0.79	9
Potassium, Dissolved combined (mg/L)	308	5.73	13.41	0.22	109	1.7	2.2	4.085	2.385	0.0	7.663	7.7	109	44
Potassium, Total Recoverable combined (mg/L)	142	4.43	6.40	0.25	44	1.2	2.35	4.375	3.175	0.0	9.138	9.6	44	17
Residue, Filterable (TDS) at 180°C (mg/L)	229	280.9	273.93	118	1770	156	170	250	94	15.0	391	416	1770	36
Silicone, Dissolved (mg/L)	17	10.11	4.30	5.5	19.2	7.2	8.9	10	2.8	3.0	14.2	18	19.2	3
Sodium, Dissolved combined (mg/L)	406	218.4	933.71	6.4	11000	44.3	49.8	81.925	37.625	0.0	138.36	140	11000	44
Sodium, Total Recoverable combined (mg/L)	155	274.9	777.39	6.4	8500	51.5	87	135	83.5	0.0	260.25	290	8500	23
Strontium, Dissolved combined (mg/L)	820	5.93	50.16	0.01	940	0.15175	0.575	1.4825	1.331	0.0	3.479	3.5	940	68
Strontium, Total Recoverable combined (mg/L)	442	4.17	26.94	0.02	410	0.37	0.92	2.1475	1.777	0.0	4.814	4.85	410	25
Sulfate (mg/L)	406	31.65	52.31	0.21	640	10	28.15	40	30	0.0	85	90	640	9
TDS (calculated) (mg/L)	141	156.8	15.11	129	244	148	155	164	16	124.0	188	201	244	3
Total Dissolved Solids (mg/L)	148	4691.8	16640.9	130	102000	307.5	605	1300	992.5	0.0	2788.75	3100	102000	24
Temperature combined (degrees C)	561	11.98	4.42	3.58	26.73	8.8889	10.6	13.58	4.691	1.9	20.62	20.7	26.73	37
Total Alkalinity as CaCO3 at pH 4.5 (mg/L)	25	110.7	23.87	72	174	96	104	125	29	52.5	168.5	174	174	1
Total Organic Carbon (TOC) (mg/L)	284	2.84	2.62	0.47	17	1.375	2.05	3	1.625	0.0	5.4375	6	17	29
Total Suspended Solids (mg/L)	213	237.0	378.78	1.9	2100	5.2	31	380	374.8	0.0	942.2	947	2100	14
Uranium, Dissolved (microgram/L)	117	8.24	14.83	0.0098	72	0.27	1.8	7.9	7.63	0.0	19.345	23	72	11

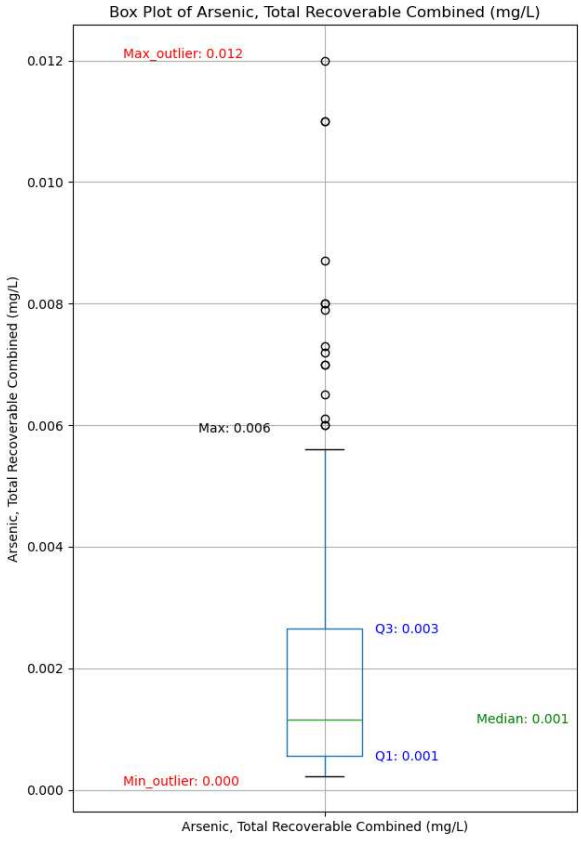
Constituent and Units	Count of Samples	Average	Standard Deviation	Minimum Concentration	Maximum Detected Concentration	First Quartile (Q1) Concentration	Median Concentration	Third Quartile (Q3) Concentration	Interquartile Range	Lower Whisker Concentration	Upper Whisker Concentration	Minimum Outlier	Maximum Outlier	Number of Outliers
Uranium, Total Recoverable (mg/L)	119	8.32	14.82	0.0098	74	0.32	2.1	8.65	8.33	0.0	21.145	23	74	11
Vanadium, Total Recoverable combined (mg/L)	148	6.11	11.73	2.50E-06	97	2.2	2.2	4.3	2.1	0.0	7.45	7.5	97	29
Zinc, Total Recoverable (mg/L)	28	0.051	0.0599	0.005	0.23	0.00875	0.03	0.08	0.071	0.0	0.187	0.22	0.23	2

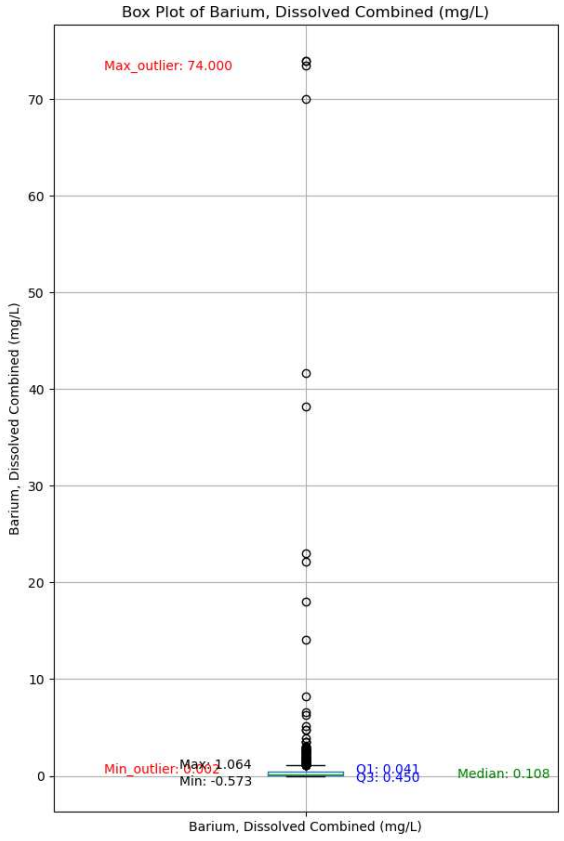
Notes:
Constituents listed as "combined" account for results that underwent conversions so units were consistent for all concentrations.
ng/L = nanograms per liter
µS/cm = microsiemens per centimeter
mg/L = milligrams per liter
SU = standard units
TDS = total dissolved solids

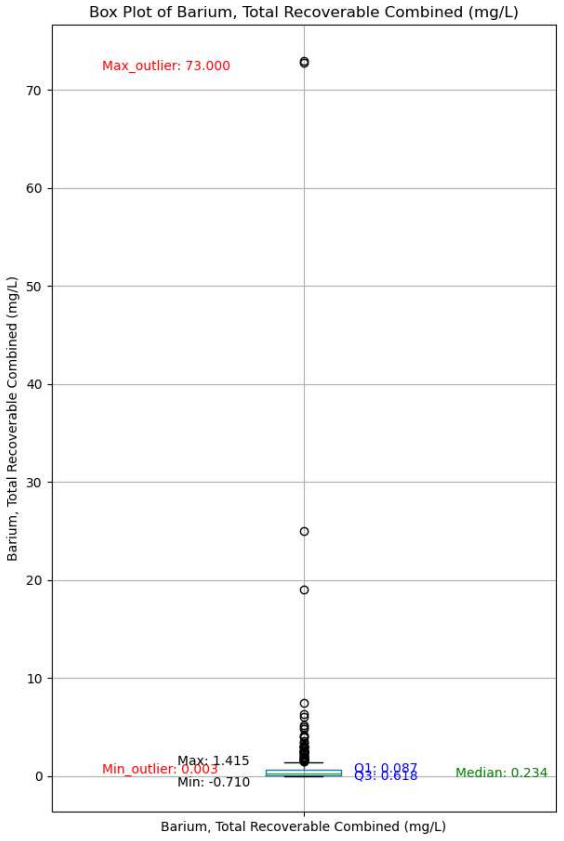

Box Plot of Alkalinity (mg/L)
Max_outlier: 770.000
Max: 402.000
Q3: 210.000
Q1: 82.000
Median: 90.150
Min_outlier: 2.000
Min: -110.000
Alkalinity (mg/L)
Alkalinity (mg/L)

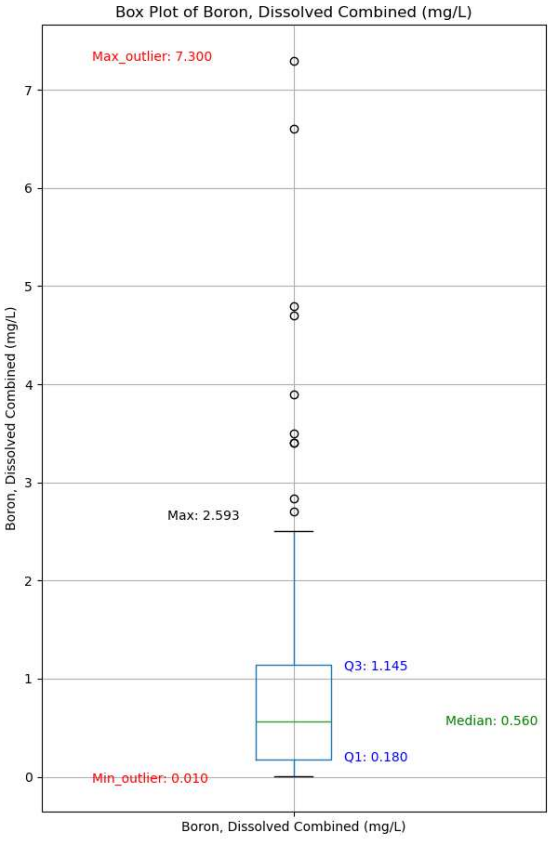

Box Plot of Aluminum, Total Recoverable Combined (mg/L)
Max_outlier: 19.000
Max: 1.131
Min_outlier: 0.025
Median: 0.067
Min: -0.639
Aluminum, Total Recoverable Combined (mg/L)
Aluminum, Total Recoverable Combined (mg/L)


Box Plot of Arsenic, Dissolved Combined (mg/L)
Max_outlier: 0.045
Max: 0.006
Q3: 0.003
Q1: 0.001
Median: 0.003
Min_outlier: 0.000
Min: -0.002
Arsenic, Dissolved Combined (mg/L)
Arsenic, Dissolved Combined (mg/L)

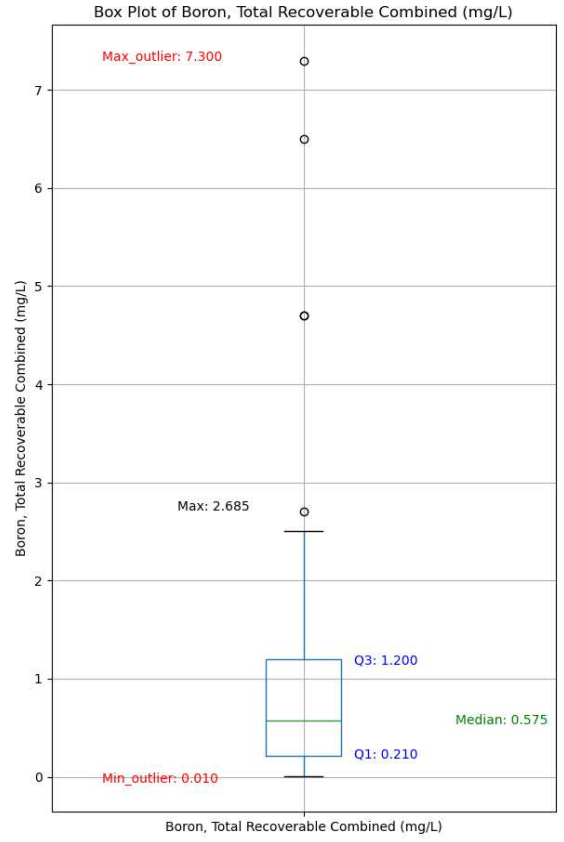

Box Plot of Arsenic, Total Recoverable Combined (mg/L)
Max_outlier: 0.012
Max: 0.006
Q3: 0.003
Median: 0.001
Q1: 0.001
Min_outlier: 0.000
Arsenic, Total Recoverable Combined (mg/L)
Arsenic, Total Recoverable Combined (mg/L)



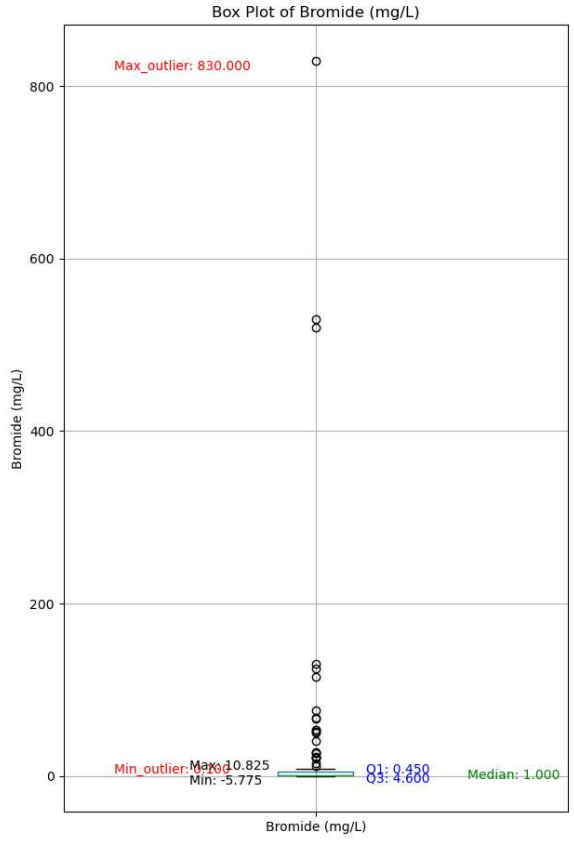


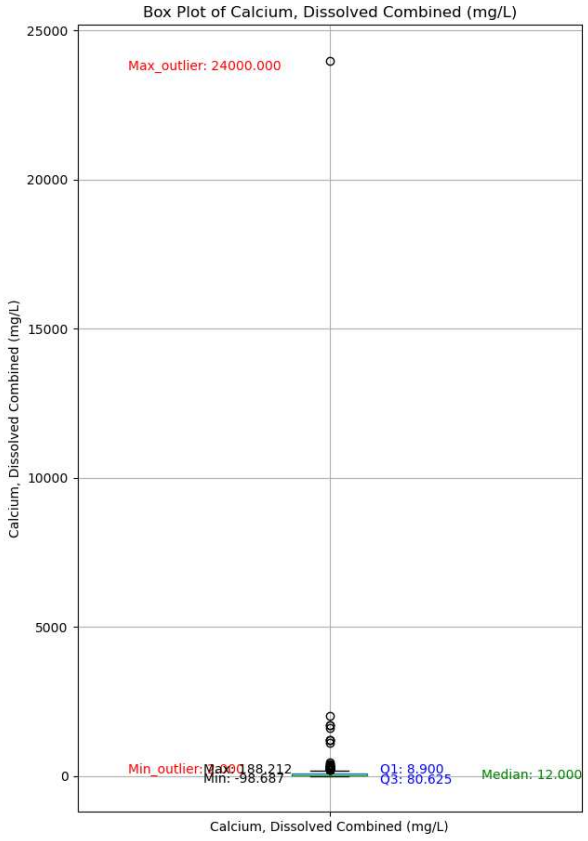


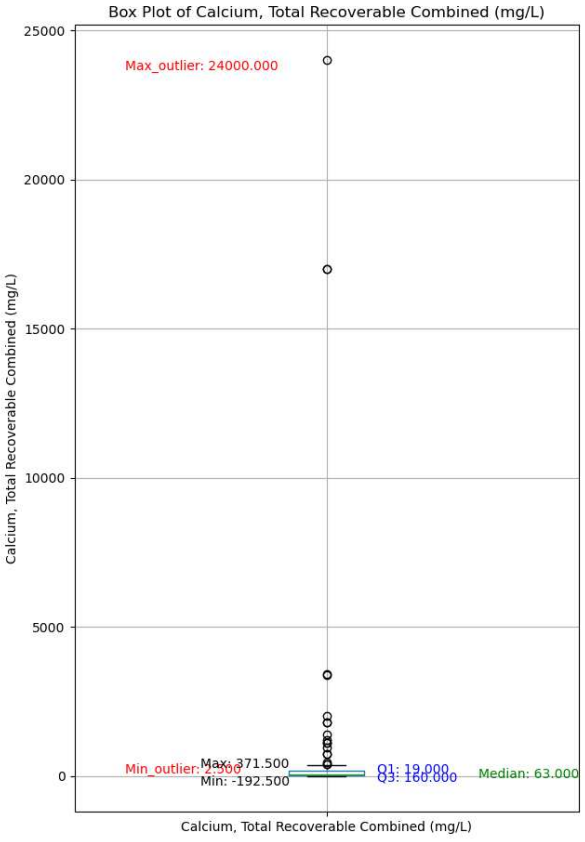
Min: -1.268

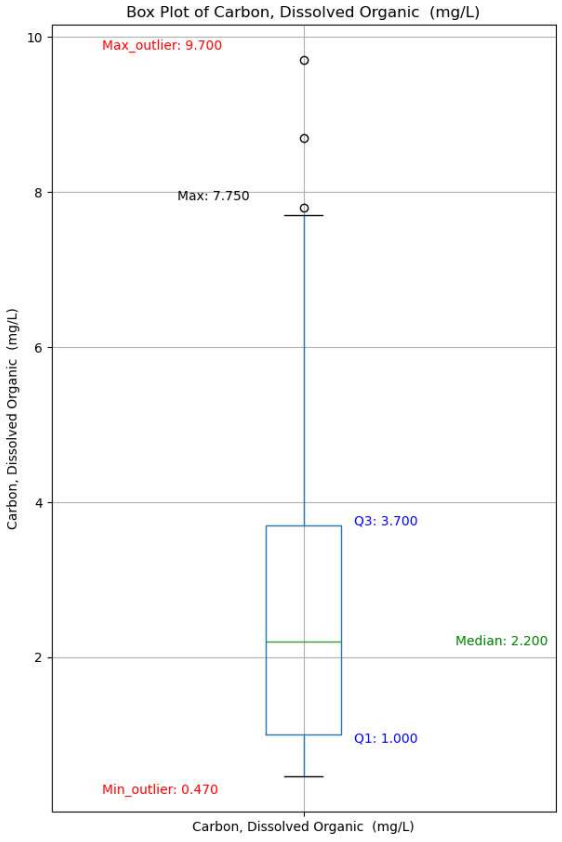


Min: -1.275

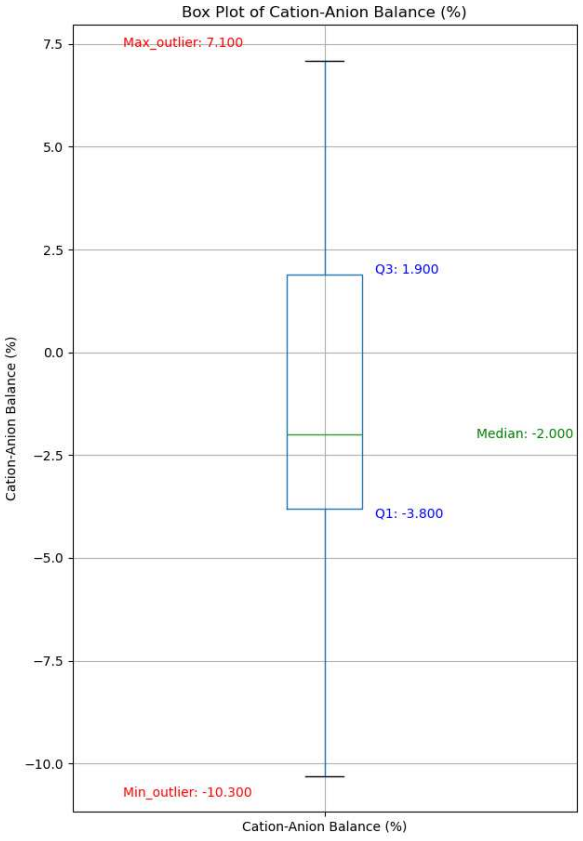

Box Plot of Bromide (mg/L)
Max_outlier: 830.000
Min_outlier: 0.100
Max: 10.825
Min: -5.775
Q1: 0.450
Q3: 4.600
Median: 1.000
Bromide (mg/L)
0
200
400
600
800


Box Plot of Calcium, Dissolved Combined (mg/L)
Max_outlier: 24000.000
Min_outlier: 0.100
Max: 188.212
Min: -98.687
Q1: 8.900
Q3: 80.625
Median: 12.000
Calcium, Dissolved Combined (mg/L)
0
5000
10000
15000
20000
25000

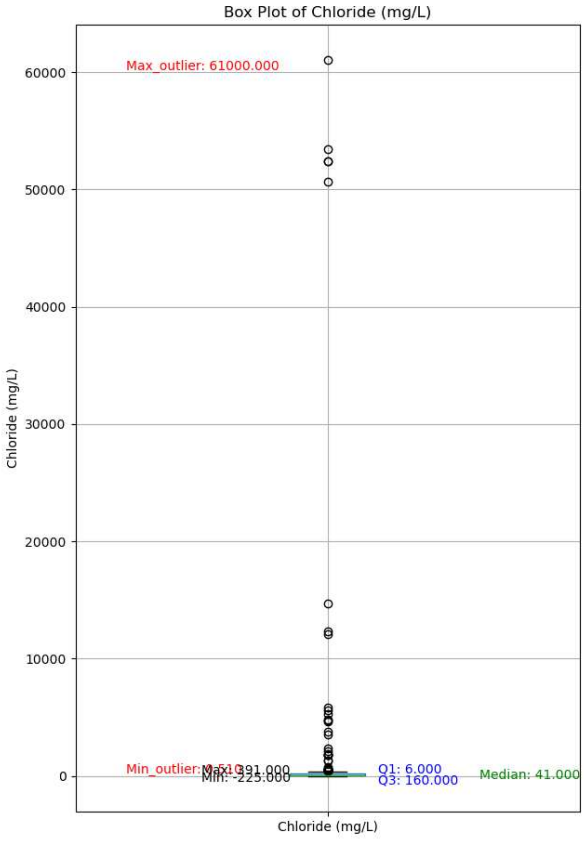

Box Plot of Calcium, Total Recoverable Combined (mg/L)
Max_outlier: 24000.000
Min_outlier: 2.500
Max: 371.500
Min: -192.500
Q1: 19.000
Q3: 160.000
Median: 63.000
Calcium, Total Recoverable Combined (mg/L)
0
5000
10000
15000
20000
25000

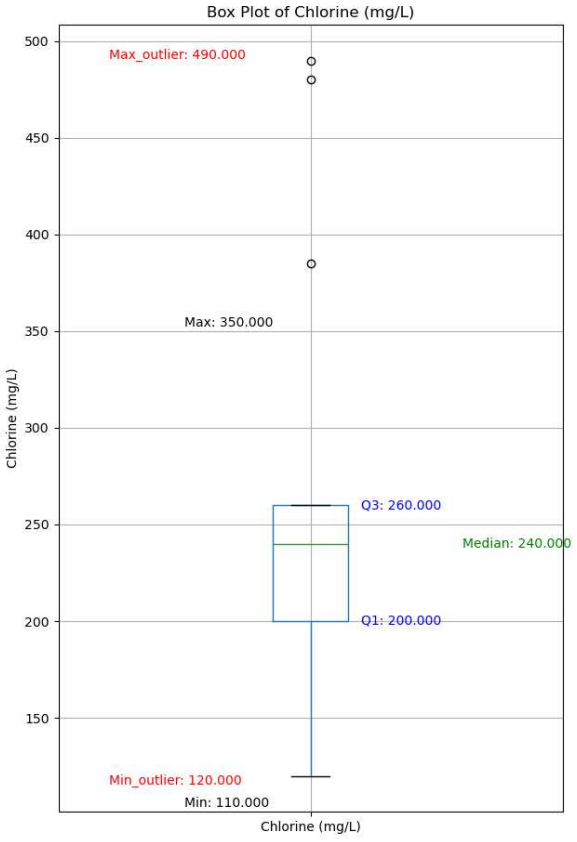

Box Plot of Carbon, Dissolved Organic (mg/L)
Max_outlier: 9.700
Max: 7.750
Q3: 3.700
Median: 2.200
Q1: 1.000
Min_outlier: 0.470
Carbon, Dissolved Organic (mg/L)
2
4
6
8
10

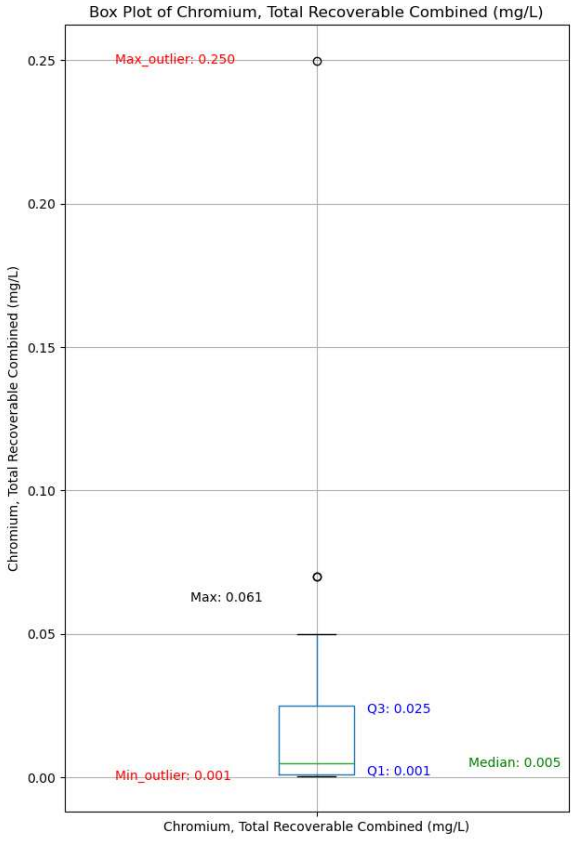
Max: 10.450



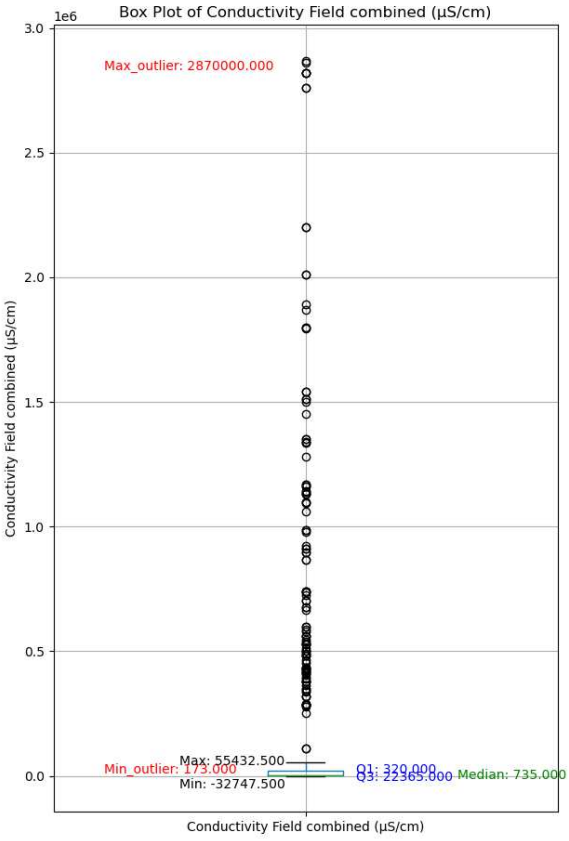
Min: -12.350

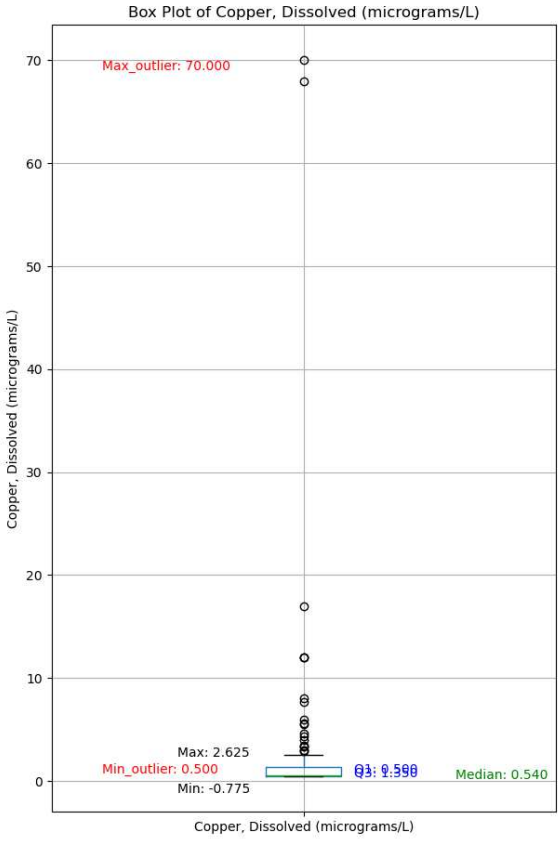


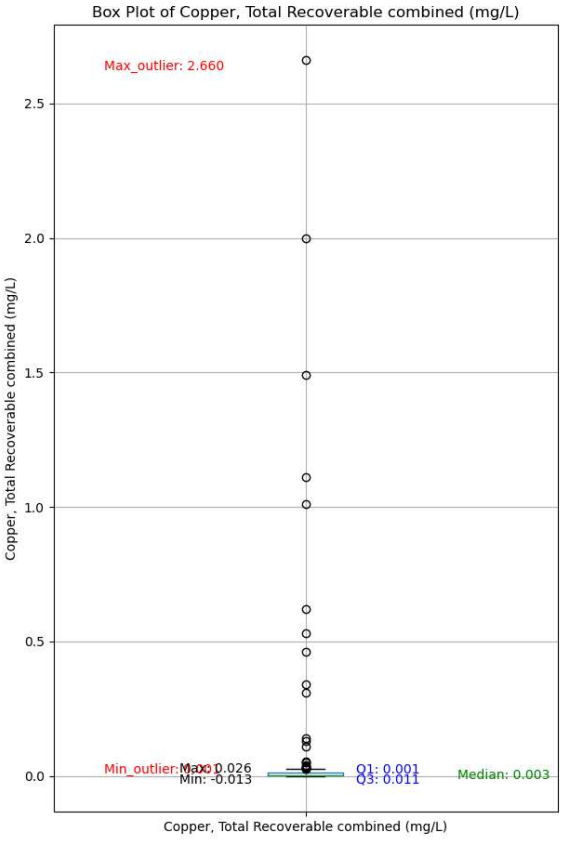


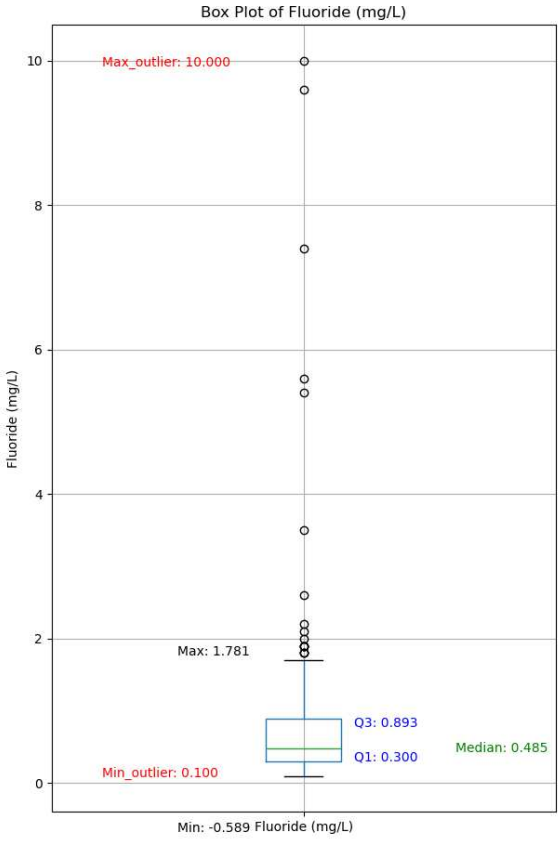


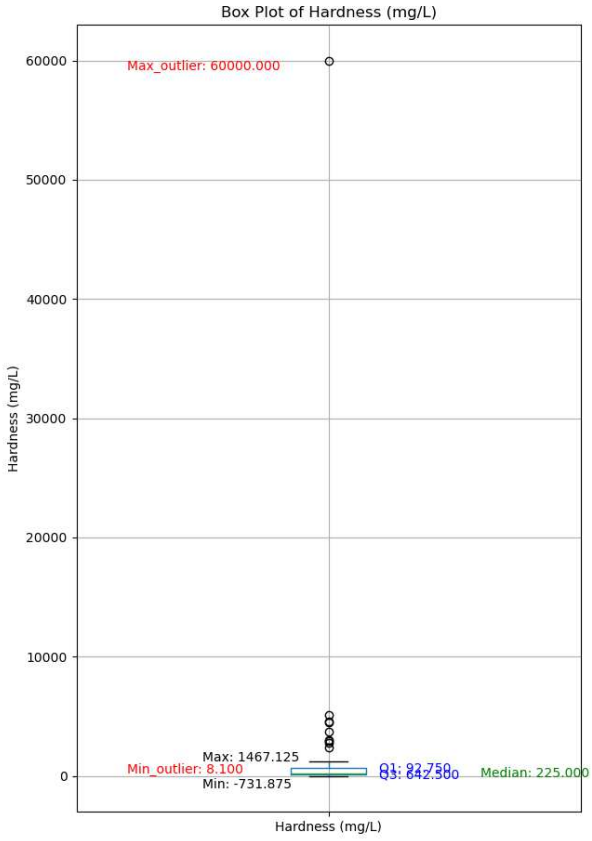
Min: -0.035

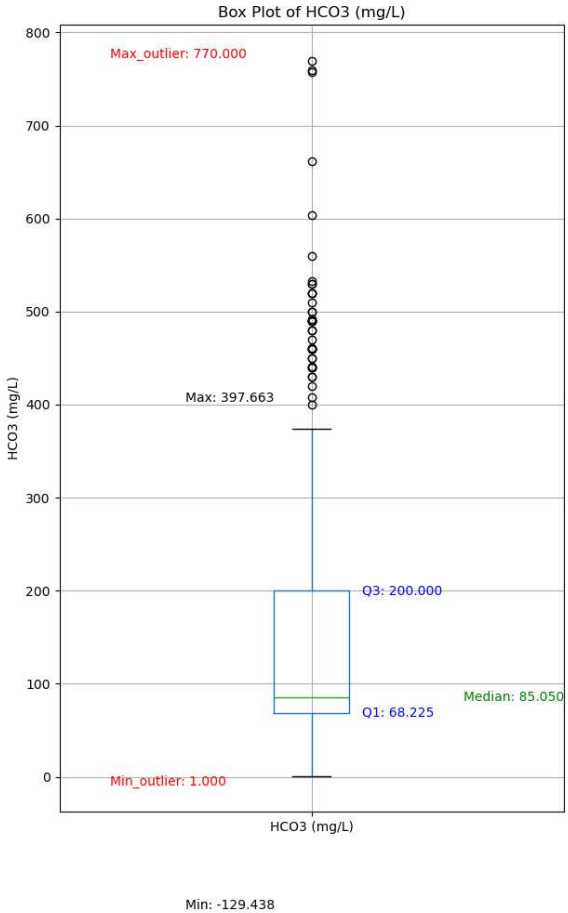

Box Plot of Conductivity Field combined (µS/cm)
1e6
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Conductivity Field combined (µS/cm)
Max_outlier: 2870000.000
Max: 55432.500
Min_outlier: 173.000
Min: -32747.500
Q1: 329.000
Q3: 22365.000
Median: 735.000
Conductivity Field combined (µS/cm)


Box Plot of Copper, Dissolved (micrograms/L)
70
60
50
40
30
20
10
0
Copper, Dissolved (micrograms/L)
Max_outlier: 70.000
Max: 2.625
Min_outlier: 0.500
Min: -0.775
Median: 0.540
Copper, Dissolved (micrograms/L)

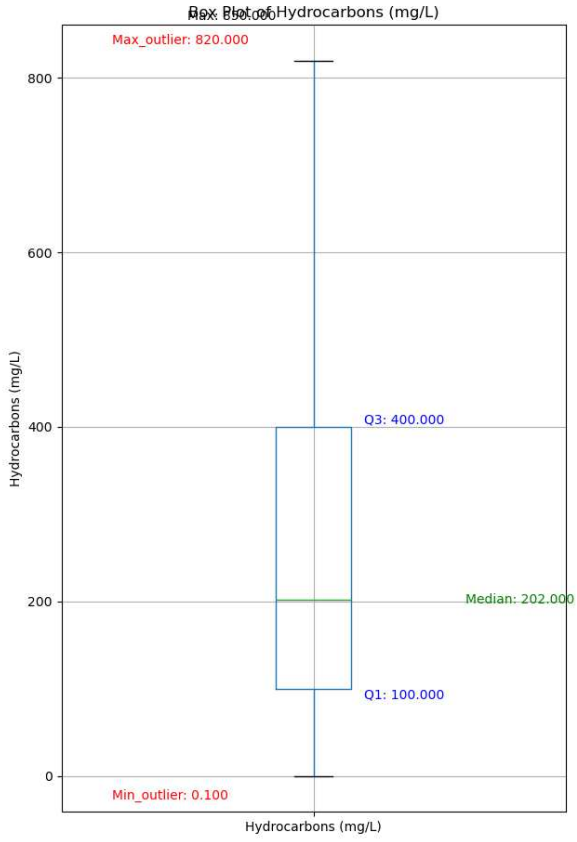

Box Plot of Copper, Total Recoverable combined (mg/L)
2.5
2.0
1.5
1.0
0.5
0.0
Copper, Total Recoverable combined (mg/L)
Max_outlier: 2.660
Max: 0.026
Min_outlier: 0.000
Min: -0.013
Q1: 0.001
Q3: 0.011
Median: 0.003
Copper, Total Recoverable combined (mg/L)

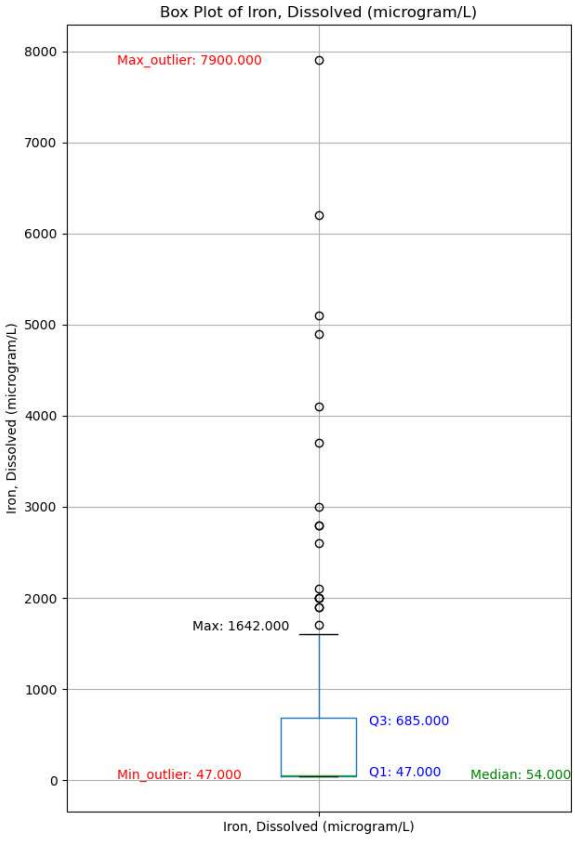

Box Plot of Fluoride (mg/L)
10
8
6
4
2
0
Fluoride (mg/L)
Max_outlier: 10.000
Max: 1.781
Q3: 0.893
Q1: 0.300
Median: 0.485
Min_outlier: 0.100
Min: -0.589 Fluoride (mg/L)



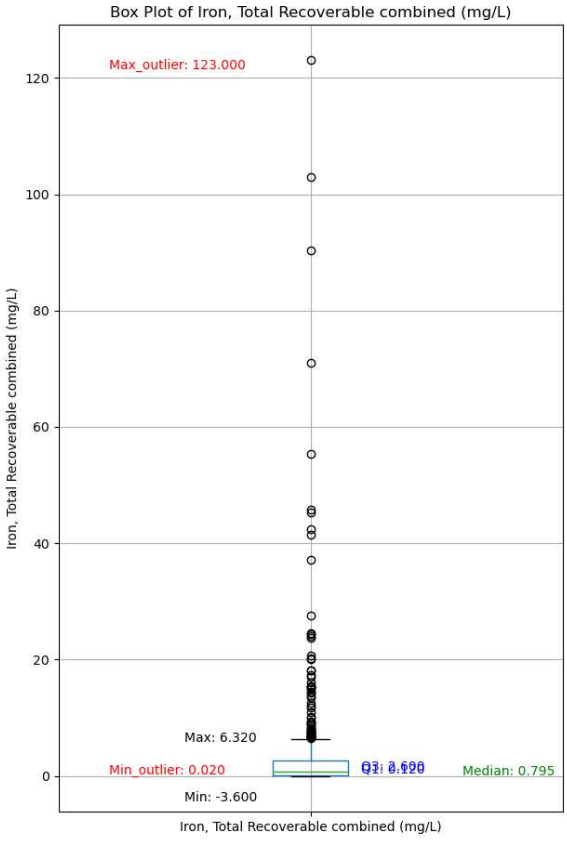


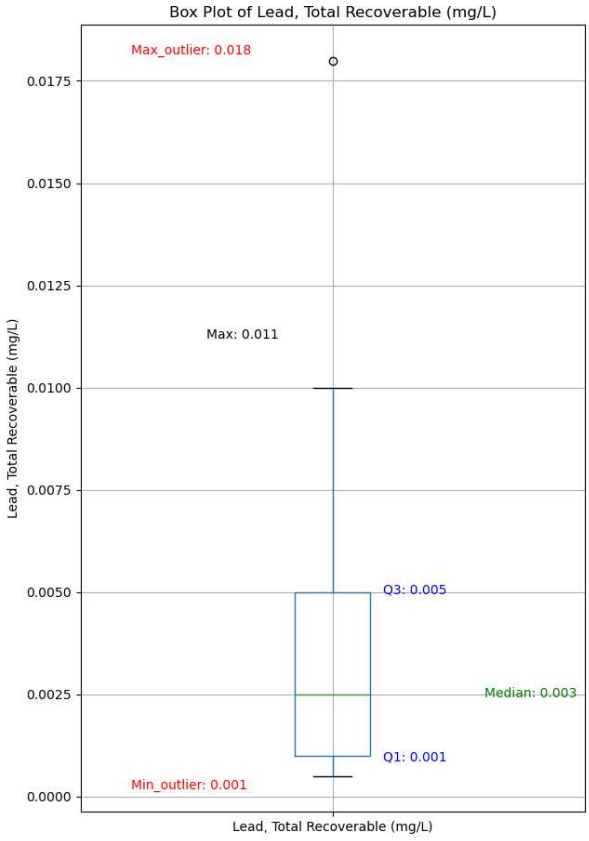
Min: -129.438

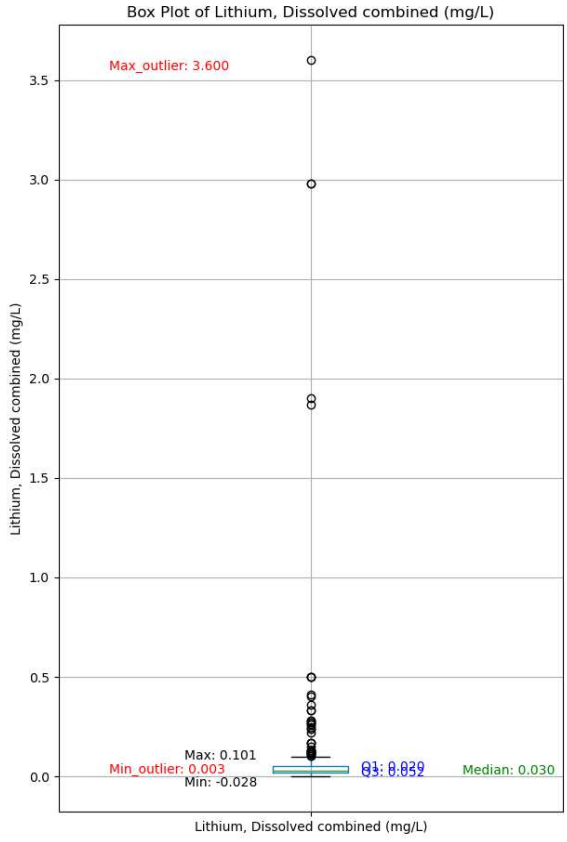


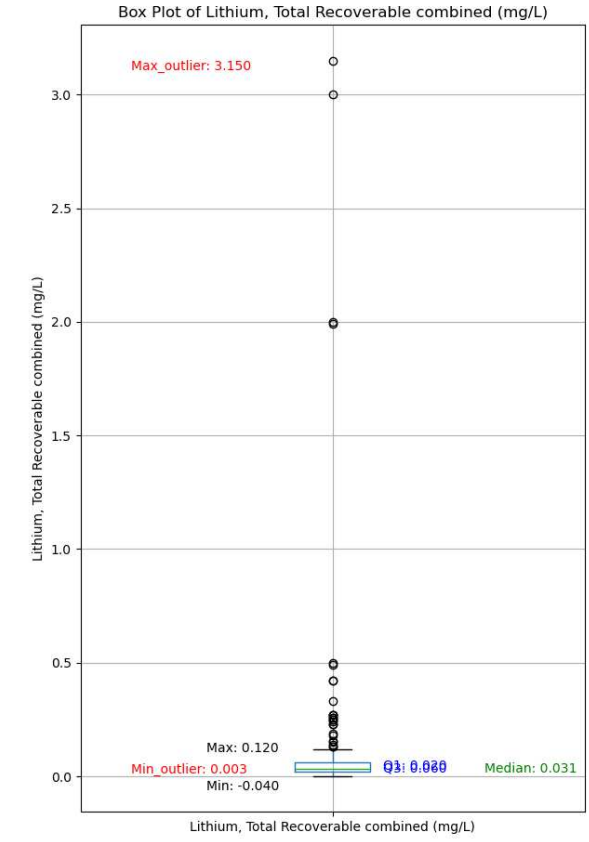


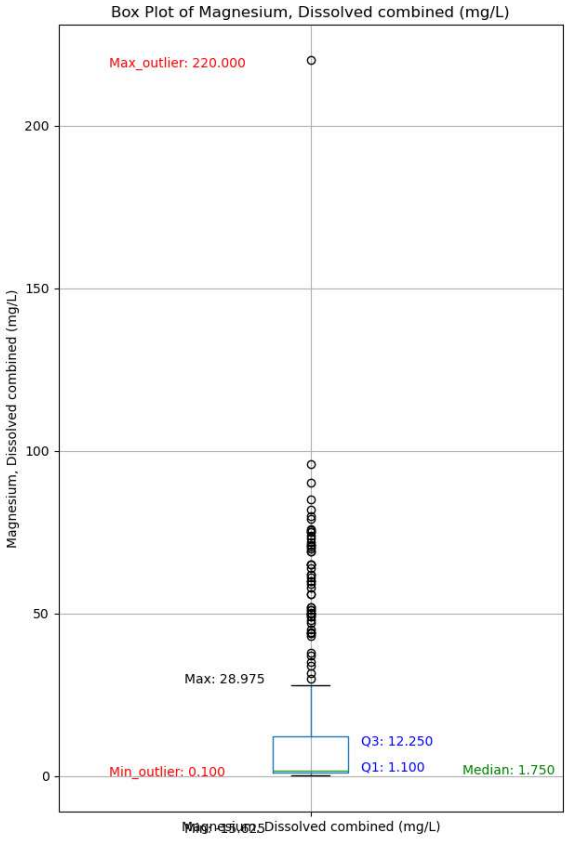
Min: -910.000

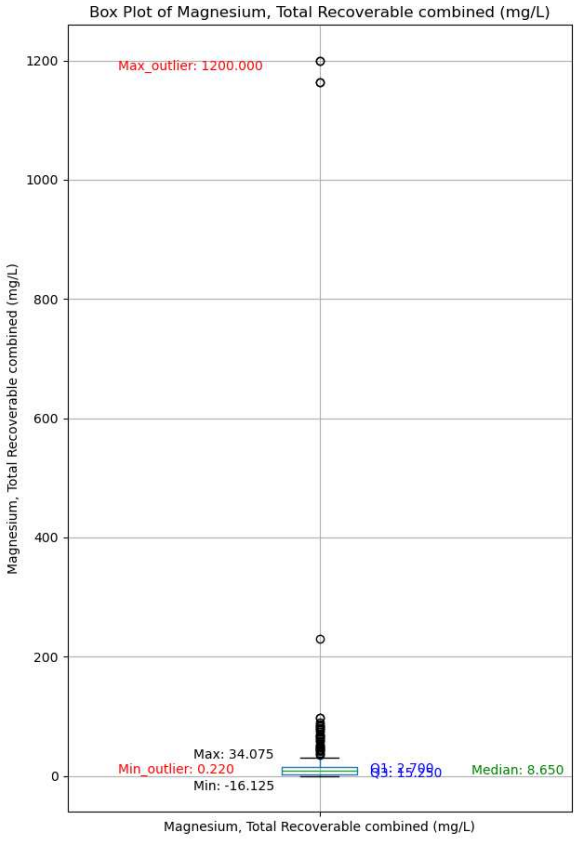

Box Plot of Iron, Total Recoverable combined (mg/L)
Max_outlier: 123.000
Max: 6.320
Min_outlier: 0.020
Median: 0.795
Min: -3.600
Iron, Total Recoverable combined (mg/L)
Iron, Total Recoverable combined (mg/L)

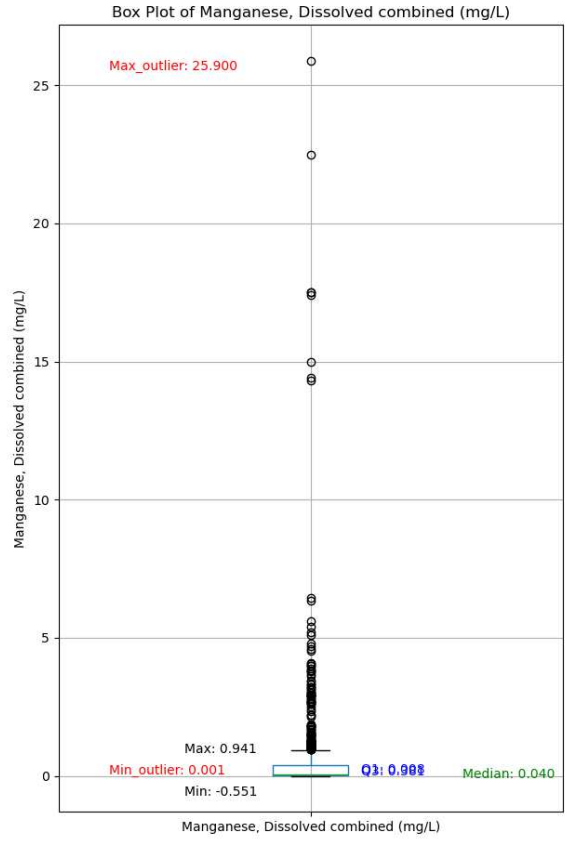

Box Plot of Lead, Total Recoverable (mg/L)
Max_outlier: 0.018
Max: 0.011
Q3: 0.005
Median: 0.003
Q1: 0.001
Min_outlier: 0.001
Lead, Total Recoverable (mg/L)
Lead, Total Recoverable (mg/L)

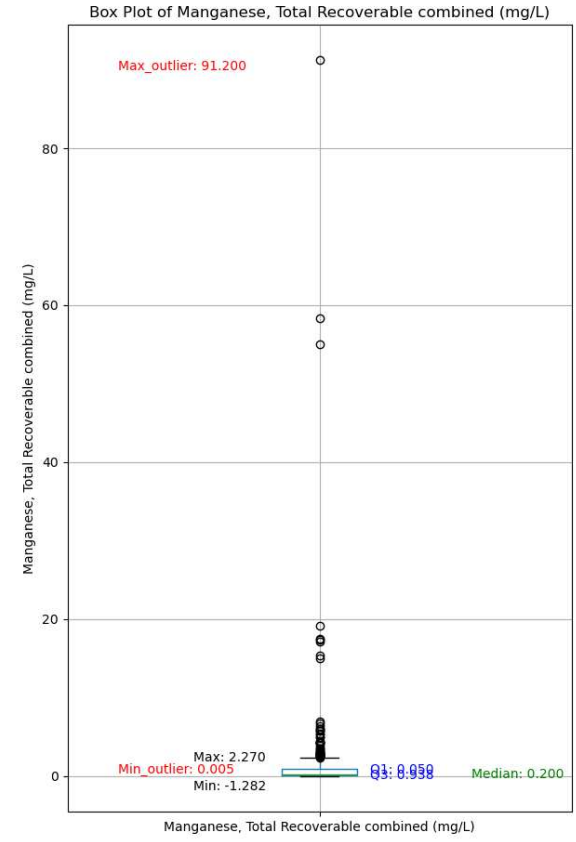

Box Plot of Lithium, Dissolved combined (mg/L)
Max_outlier: 3.600
Max: 0.101
Min_outlier: 0.003
Median: 0.030
Min: -0.028
Lithium, Dissolved combined (mg/L)
Lithium, Dissolved combined (mg/L)

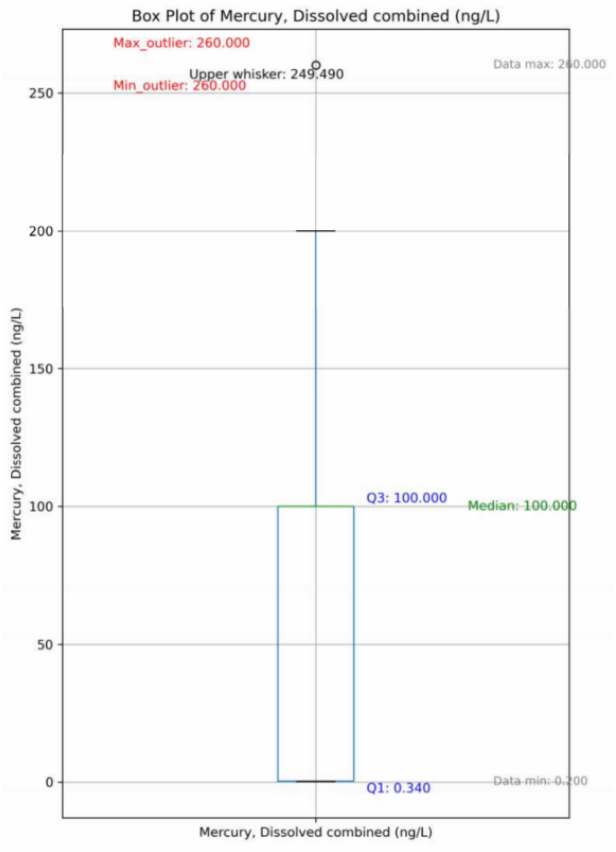

Box Plot of Lithium, Total Recoverable combined (mg/L)
Max_outlier: 3.150
Max: 0.120
Min_outlier: 0.003
Median: 0.031
Min: -0.040
Lithium, Total Recoverable combined (mg/L)
Lithium, Total Recoverable combined (mg/L)

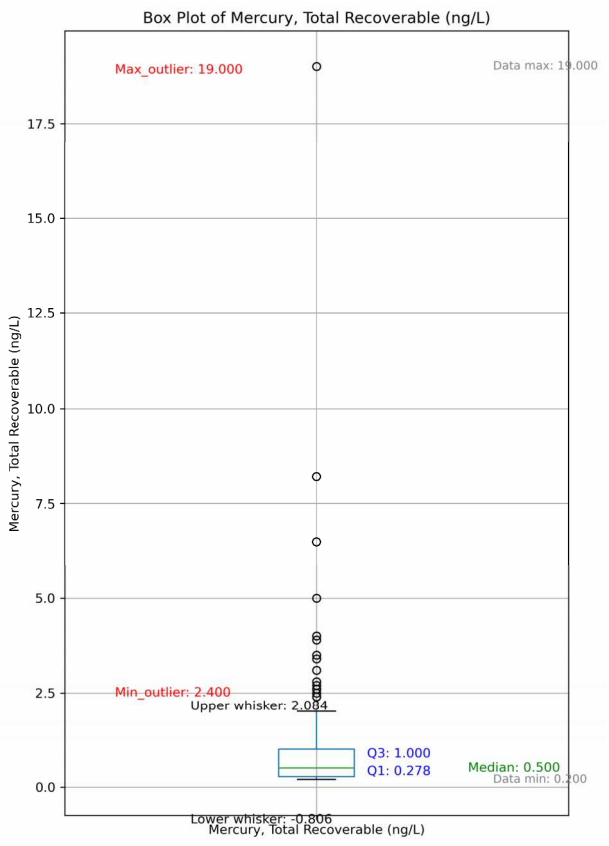

Box Plot of Magnesium, Dissolved combined (mg/L)
Max_outlier: 220.000
Max: 28.975
Q3: 12.250
Q1: 1.100
Min_outlier: 0.100
Median: 1.750
Magnesium, Dissolved combined (mg/L)
Magnesium, Dissolved combined (mg/L)

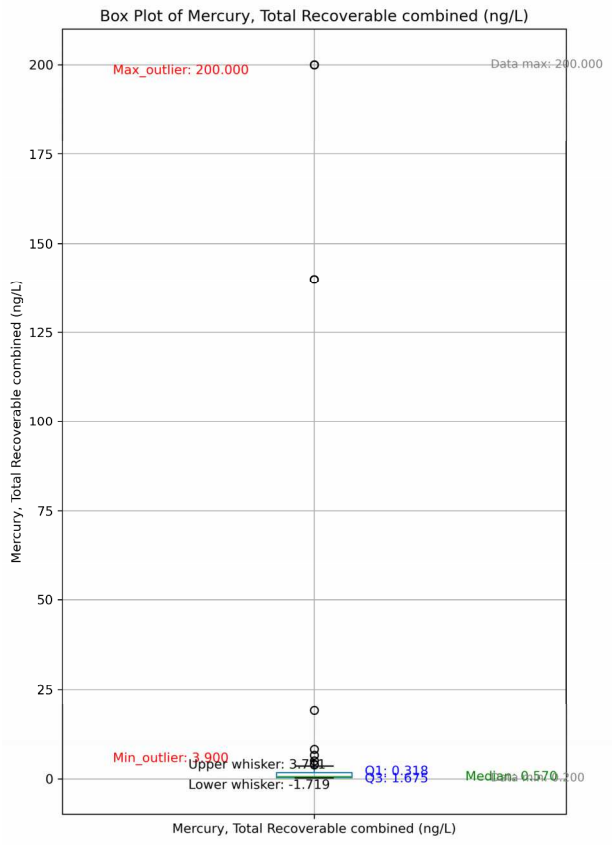

Box Plot of Magnesium, Total Recoverable combined (mg/L)
Max_outlier: 1200.000
Max: 34.075
Min_outlier: 0.220
Min: -16.125
Median: 8.650
Magnesium, Total Recoverable combined (mg/L)
Magnesium, Total Recoverable combined (mg/L)

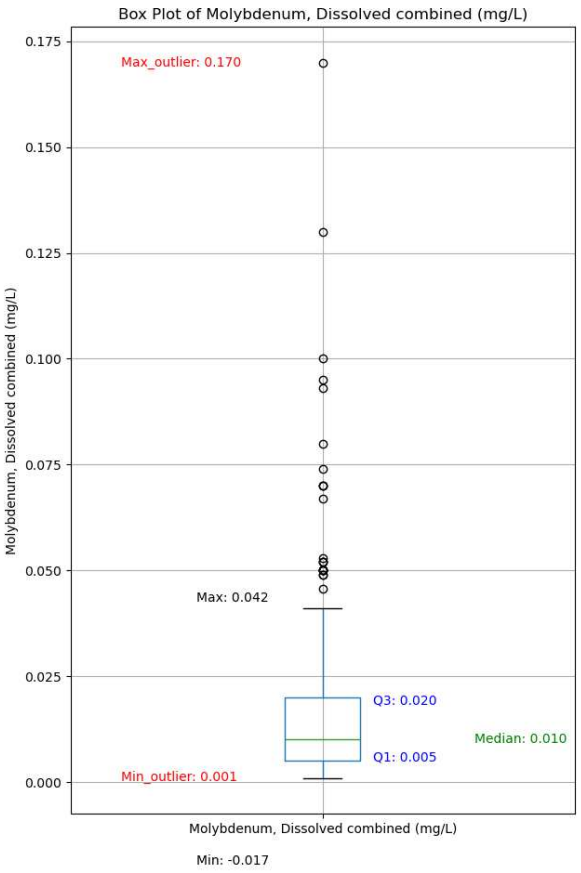

Box Plot of Manganese, Dissolved combined (mg/L)
Max_outlier: 25.900
Max: 0.941
Min_outlier: 0.001
Min: -0.551
Median: 0.040
Manganese, Dissolved combined (mg/L)
Manganese, Dissolved combined (mg/L)

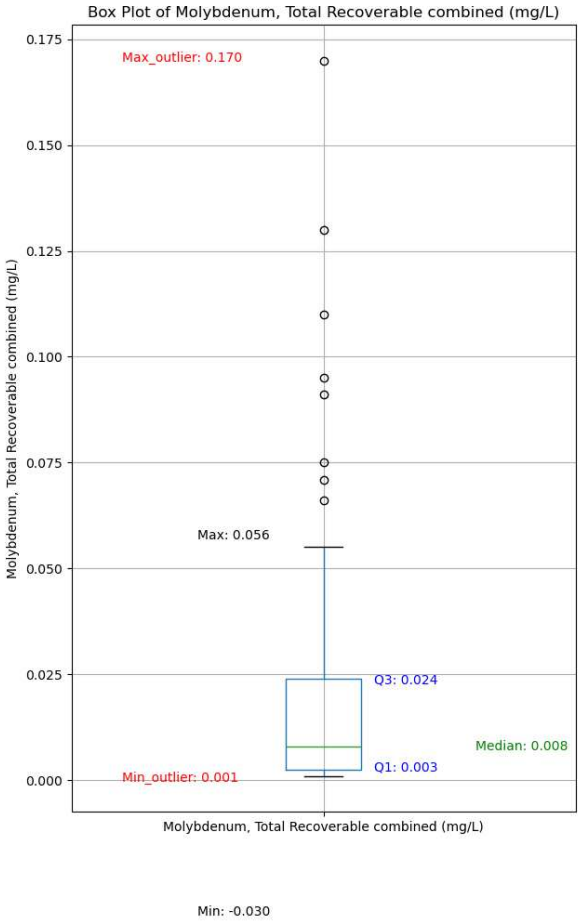

Box Plot of Manganese, Total Recoverable combined (mg/L)
Max_outlier: 91.200
Max: 2.270
Min_outlier: 0.005
Min: -1.282
Median: 0.200
Manganese, Total Recoverable combined (mg/L)
Manganese, Total Recoverable combined (mg/L)

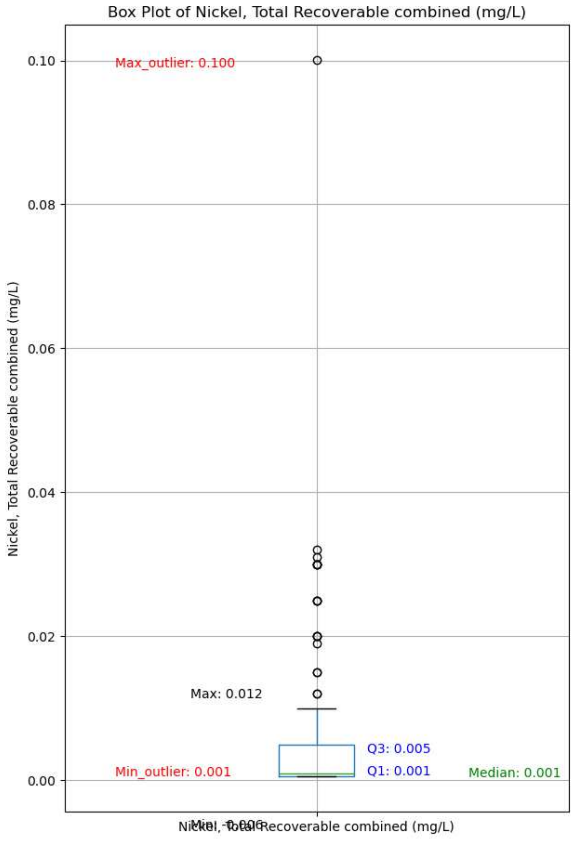

Box Plot of Mercury, Dissolved combined (ng/L)
Max_outlier: 260.000
Min_outlier: 260.000
Upper whisker: 249.490
Data max: 260.000
Q3: 100.000
Median: 100.000
Q1: 0.340
Data min: 0.200
Mercury, Dissolved combined (ng/L)
Mercury, Dissolved combined (ng/L)

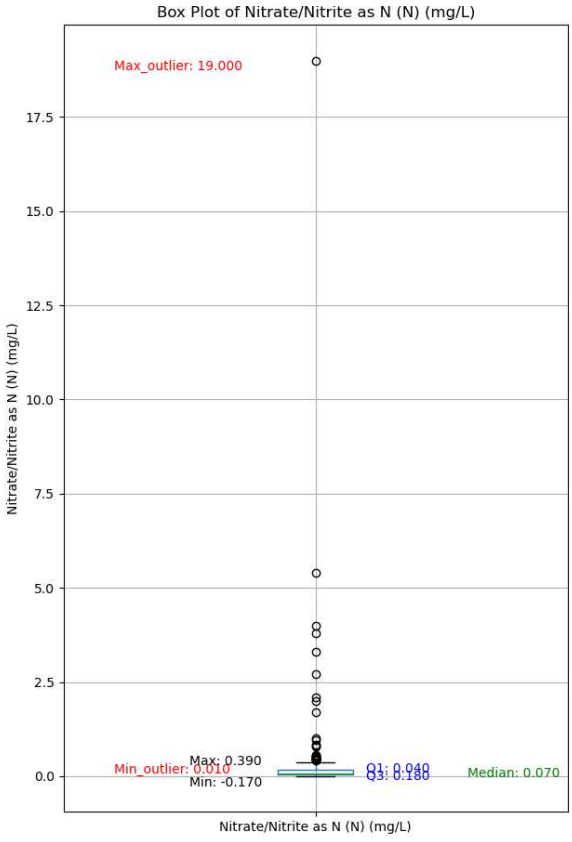

Box Plot of Mercury, Total Recoverable (ng/L)
Max_outlier: 19.000
Data max: 19.000
Min_outlier: 2.400
Upper whisker: 2.064
Q3: 1.000
Q1: 0.278
Median: 0.500
Data min: 0.200
Lower whisker: -0.806
Mercury, Total Recoverable (ng/L)
Mercury, Total Recoverable (ng/L)

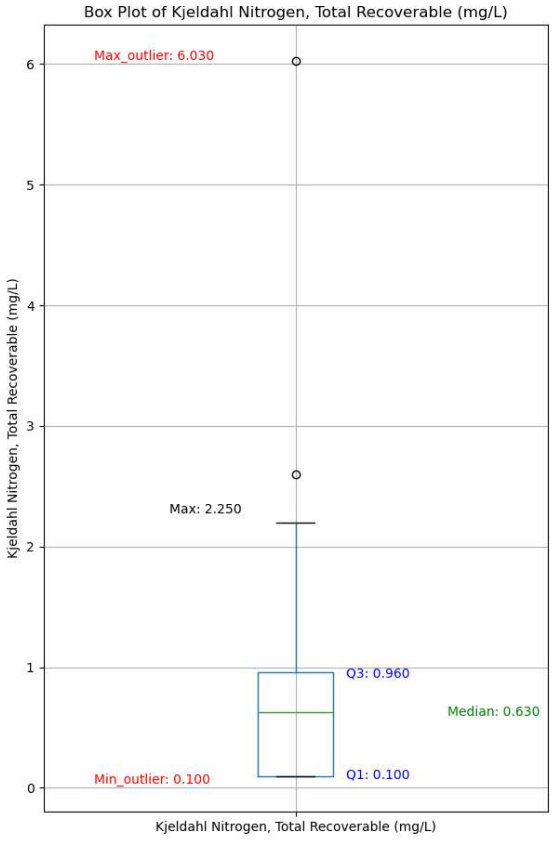

Box Plot of Mercury, Total Recoverable combined (ng/L)
Max_outlier: 200.000
Data max: 200.000
Min_outlier: 3.900
Upper whisker: 3.761
Q1: 0.318
Q3: 1.675
Median: 0.570
Lower whisker: -1.719
Mercury, Total Recoverable combined (ng/L)
Mercury, Total Recoverable combined (ng/L)

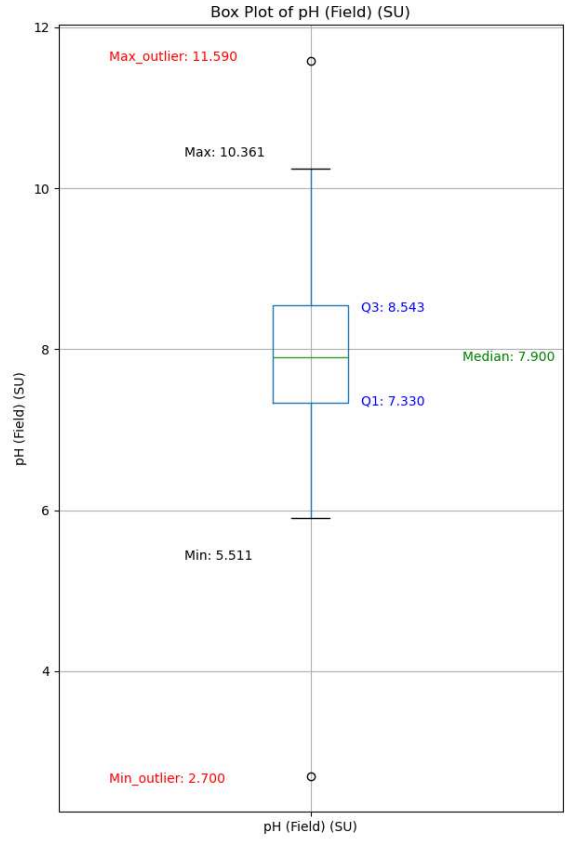

Box Plot of Molybdenum, Dissolved combined (mg/L)
Max_outlier: 0.170
Max: 0.042
Q3: 0.020
Median: 0.010
Q1: 0.005
Min_outlier: 0.001
Molybdenum, Dissolved combined (mg/L)
Molybdenum, Dissolved combined (mg/L)
Min: -0.017

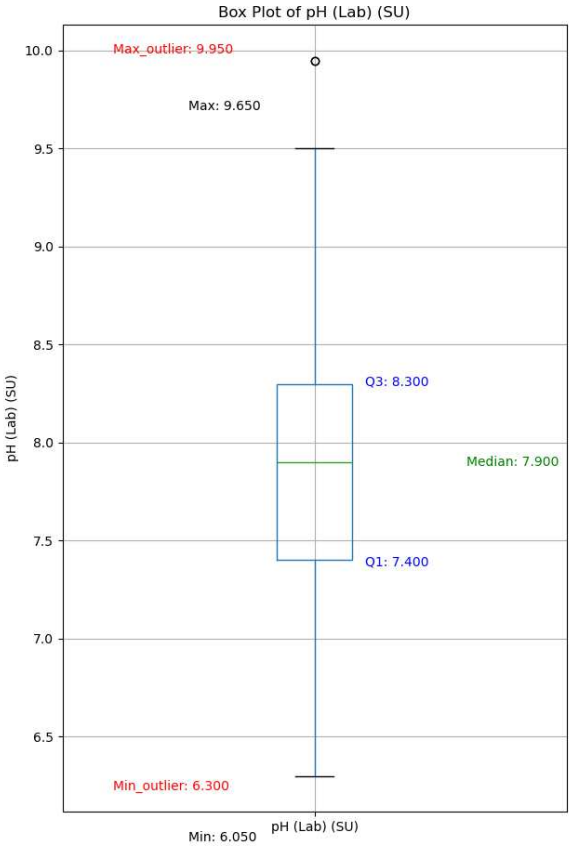

Box Plot of Molybdenum, Total Recoverable combined (mg/L)
Molybdenum, Total Recoverable combined (mg/L)
Max_outlier: 0.170
Max: 0.056
Q3: 0.024
Median: 0.008
Q1: 0.003
Min_outlier: 0.001
Min: -0.030
Molybdenum, Total Recoverable combined (mg/L)

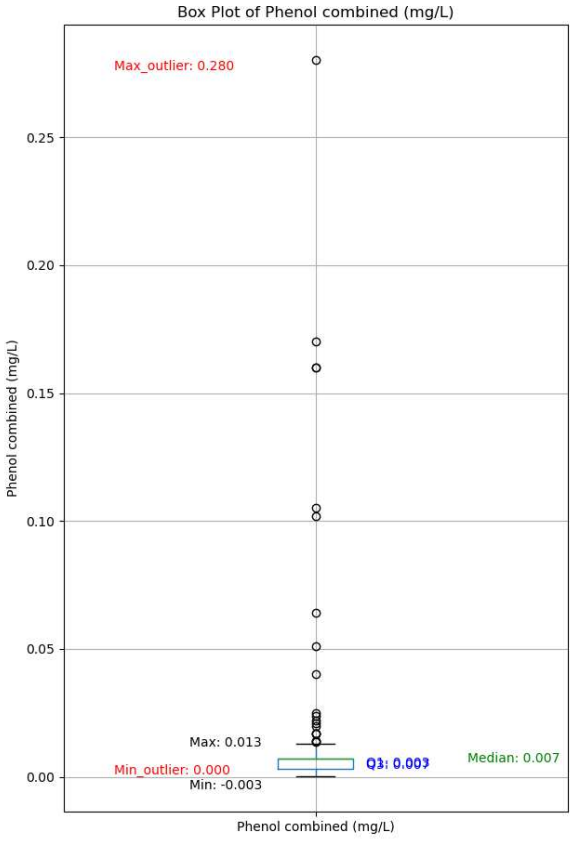

Box Plot of Nickel, Total Recoverable combined (mg/L)
Nickel, Total Recoverable combined (mg/L)
Max_outlier: 0.100
Max: 0.012
Q3: 0.005
Q1: 0.001
Median: 0.001
Min_outlier: 0.001
Nickel, Total Recoverable combined (mg/L)

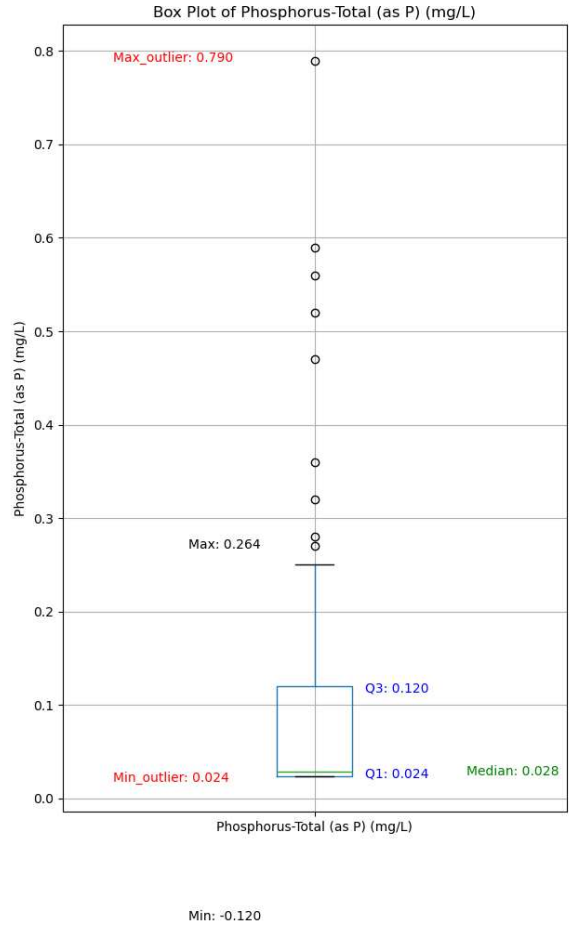

Box Plot of Nitrate/Nitrite as N (N) (mg/L)
Nitrate/Nitrite as N (N) (mg/L)
Max_outlier: 19.000
Max: 0.390
Q1: 0.040
Q3: 0.100
Median: 0.070
Min_outlier: 0.010
Min: -0.170
Nitrate/Nitrite as N (N) (mg/L)

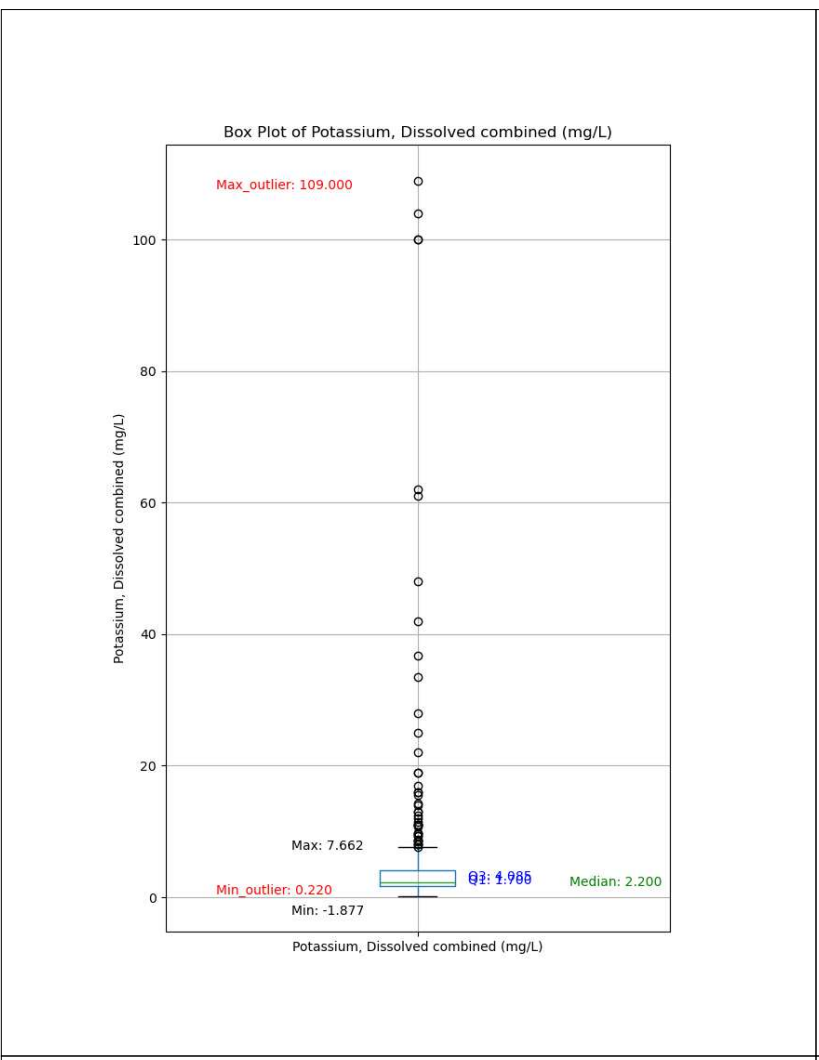

Box Plot of Kjeldahl Nitrogen, Total Recoverable (mg/L)
Kjeldahl Nitrogen, Total Recoverable (mg/L)
Max_outlier: 6.030
Max: 2.250
Q3: 0.960
Median: 0.630
Q1: 0.100
Min_outlier: 0.100
Kjeldahl Nitrogen, Total Recoverable (mg/L)

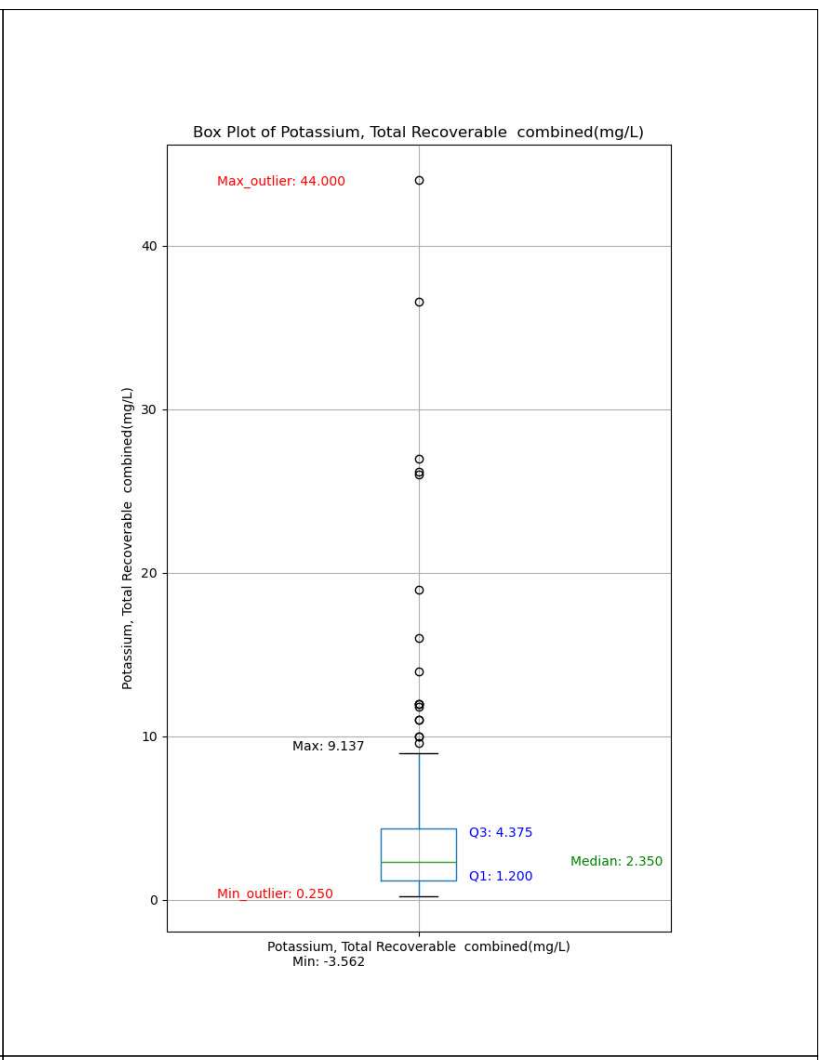

Box Plot of pH (Field) (SU)
Max_outlier: 11.590
Max: 10.361
Q3: 8.543
Median: 7.900
Q1: 7.330
Min: 5.511
Min_outlier: 2.700
pH (Field) (SU)
pH (Field) (SU)

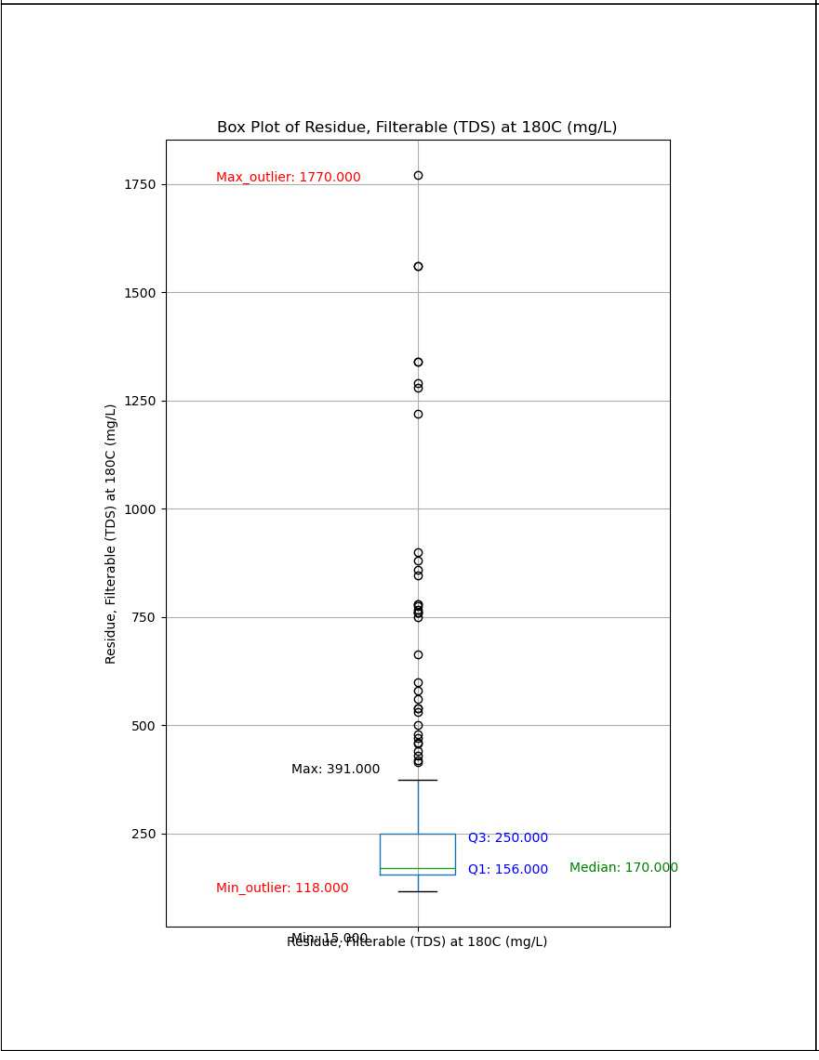

Box Plot of pH (Lab) (SU)
Max_outlier: 9.950
Max: 9.650
Q3: 8.300
Median: 7.900
Q1: 7.400
Min_outlier: 6.300
Min: 6.050
pH (Lab) (SU)
pH (Lab) (SU)

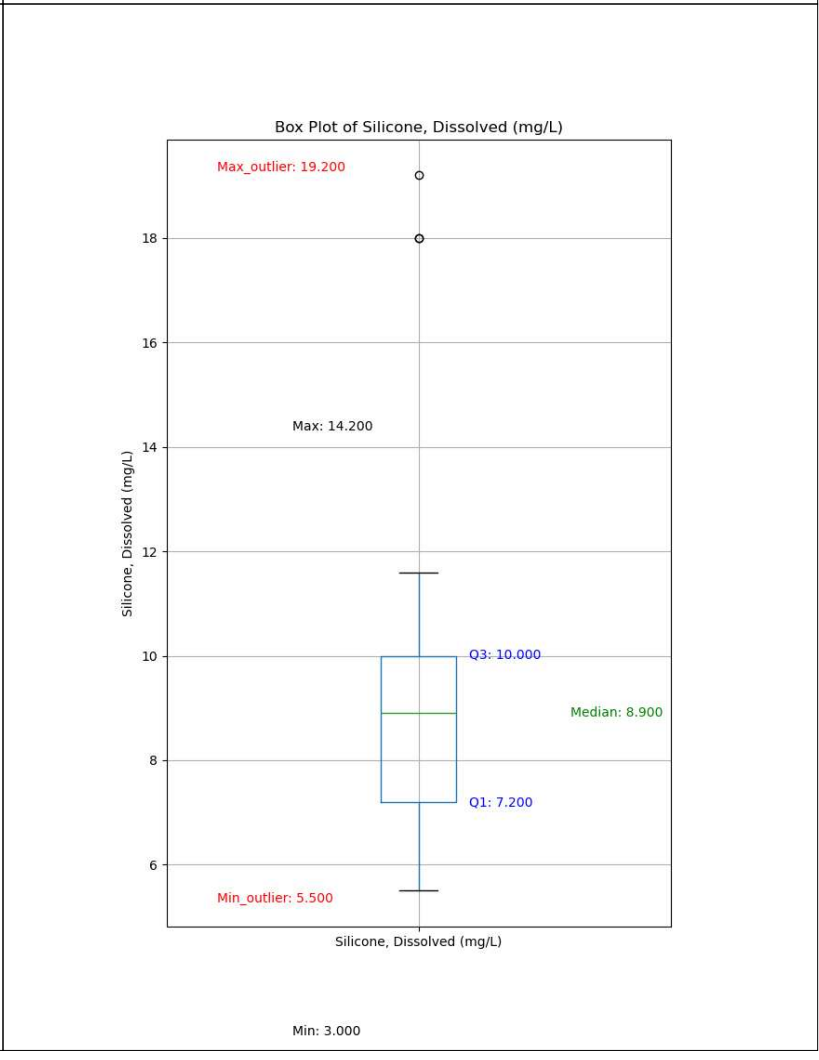

Box Plot of Phenol combined (mg/L)
Max_outlier: 0.280
Max: 0.013
Min_outlier: 0.000
Min: -0.003
Median: 0.007
Phenol combined (mg/L)
Phenol combined (mg/L)

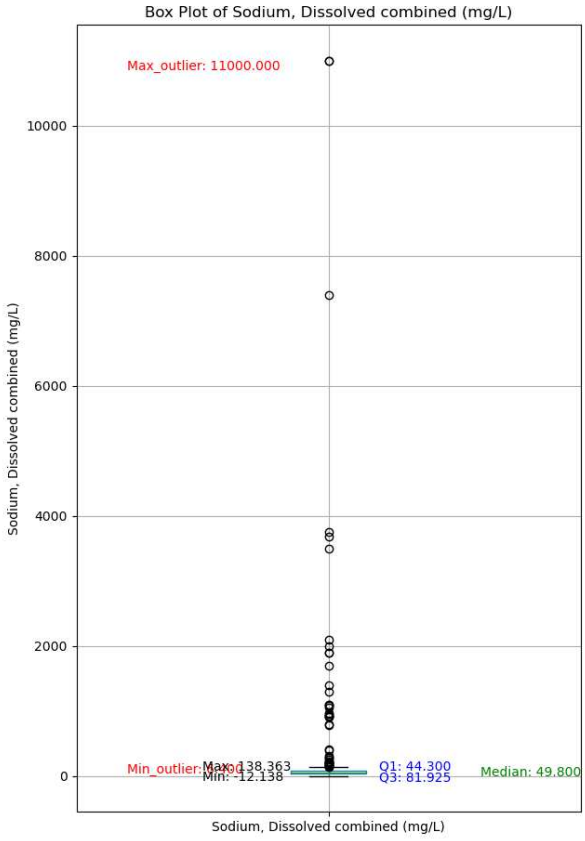

Box Plot of Phosphorus-Total (as P) (mg/L)
Max_outlier: 0.790
Max: 0.264
Q3: 0.120
Min_outlier: 0.024
Q1: 0.024
Median: 0.028
Min: -0.120
Phosphorus-Total (as P) (mg/L)
Phosphorus-Total (as P) (mg/L)

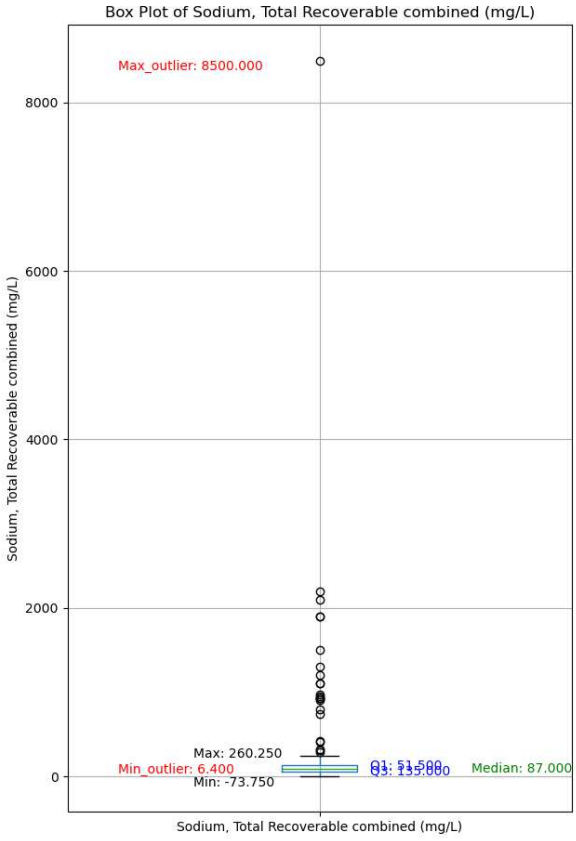

Box Plot of Potassium, Dissolved combined (mg/L)
Max_outlier: 109.000
Max: 7.662
Min_outlier: 0.220
Min: -1.877
Median: 2.200
Potassium, Dissolved combined (mg/L)
Potassium, Dissolved combined (mg/L)

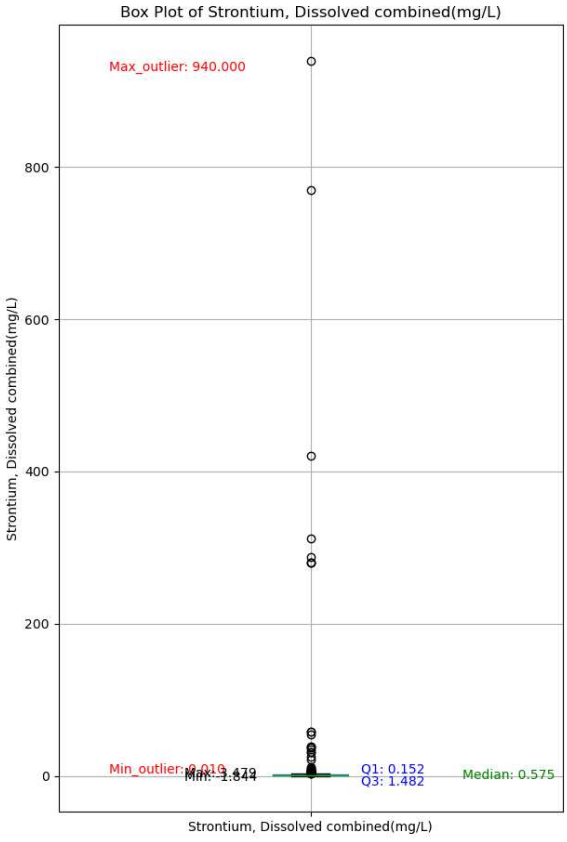

Box Plot of Potassium, Total Recoverable combined(mg/L)
Max_outlier: 44.000
Max: 9.137
Q3: 4.375
Q1: 1.200
Median: 2.350
Min_outlier: 0.250
Min: -3.562
Potassium, Total Recoverable combined(mg/L)
Potassium, Total Recoverable combined(mg/L)

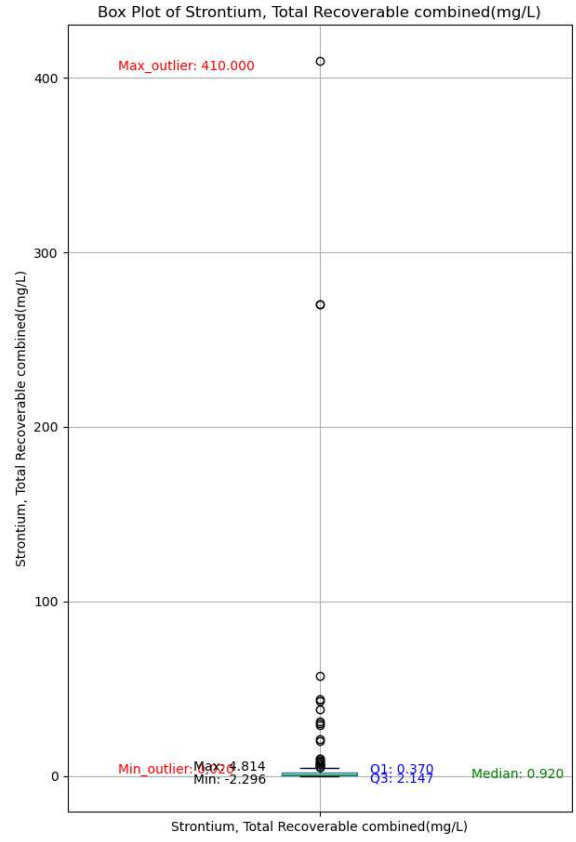

Box Plot of Residue, Filterable (TDS) at 180C (mg/L)
Max_outlier: 1770.000
Max: 391.000
Q3: 250.000
Q1: 156.000
Median: 170.000
Min_outlier: 118.000
Min: 15.000
Residue, Filterable (TDS) at 180C (mg/L)
Residue, Filterable (TDS) at 180C (mg/L)

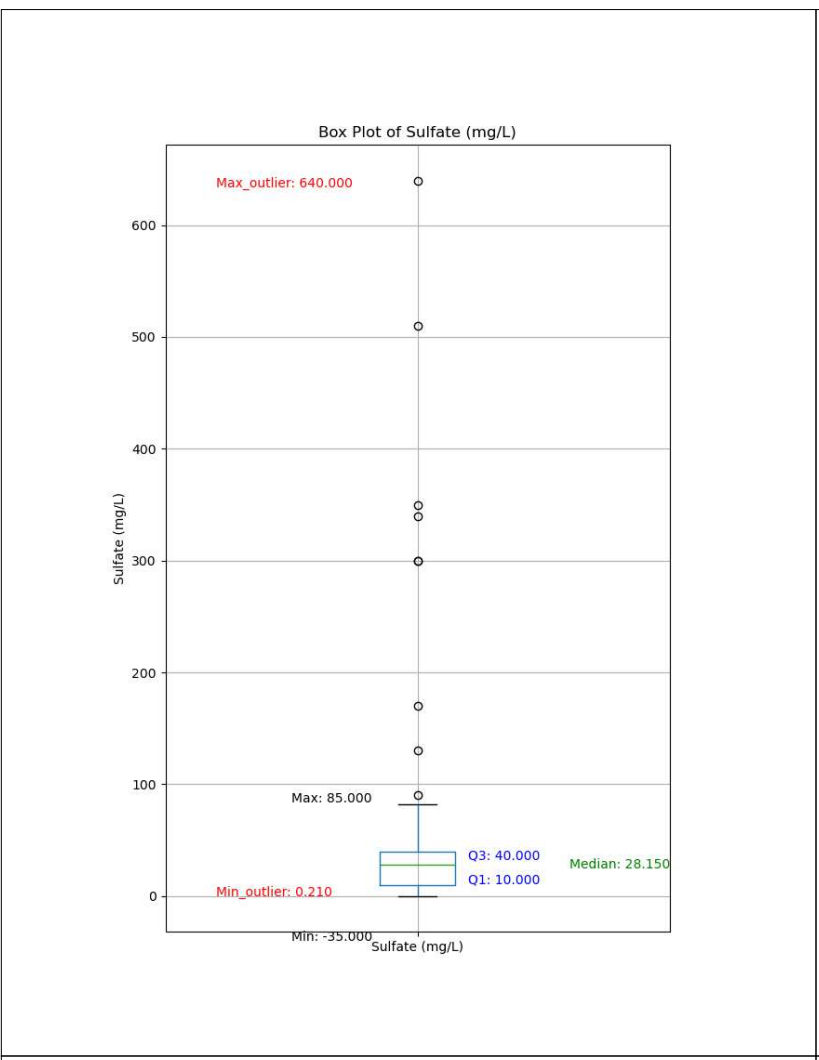

Box Plot of Silicone, Dissolved (mg/L)
Max_outlier: 19.200
Max: 14.200
Q3: 10.000
Q1: 7.200
Median: 8.900
Min_outlier: 5.500
Min: 3.000
Silicone, Dissolved (mg/L)
Silicone, Dissolved (mg/L)

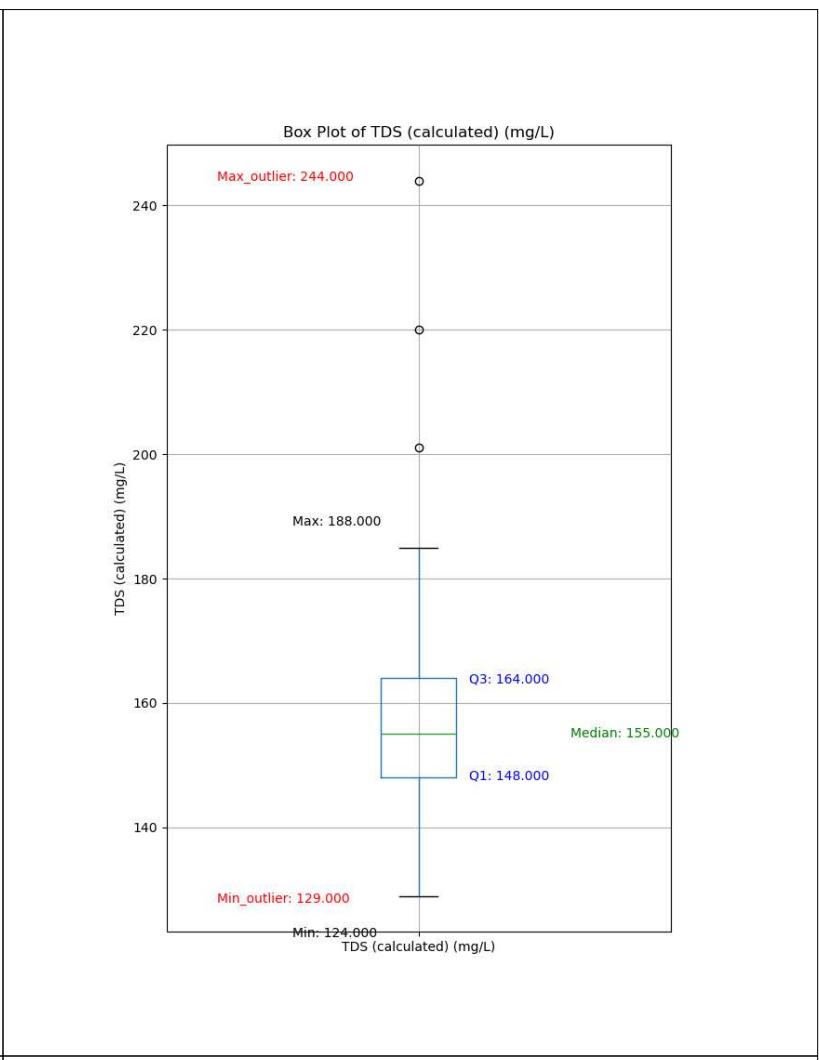

Box Plot of Sodium, Dissolved combined (mg/L)
Max_outlier: 11000.000
Min_outlier: 0.000
Max: 138.363
Min: -12.138
Q1: 44.300
Q3: 81.925
Median: 49.800
Sodium, Dissolved combined (mg/L)
Sodium, Dissolved combined (mg/L)

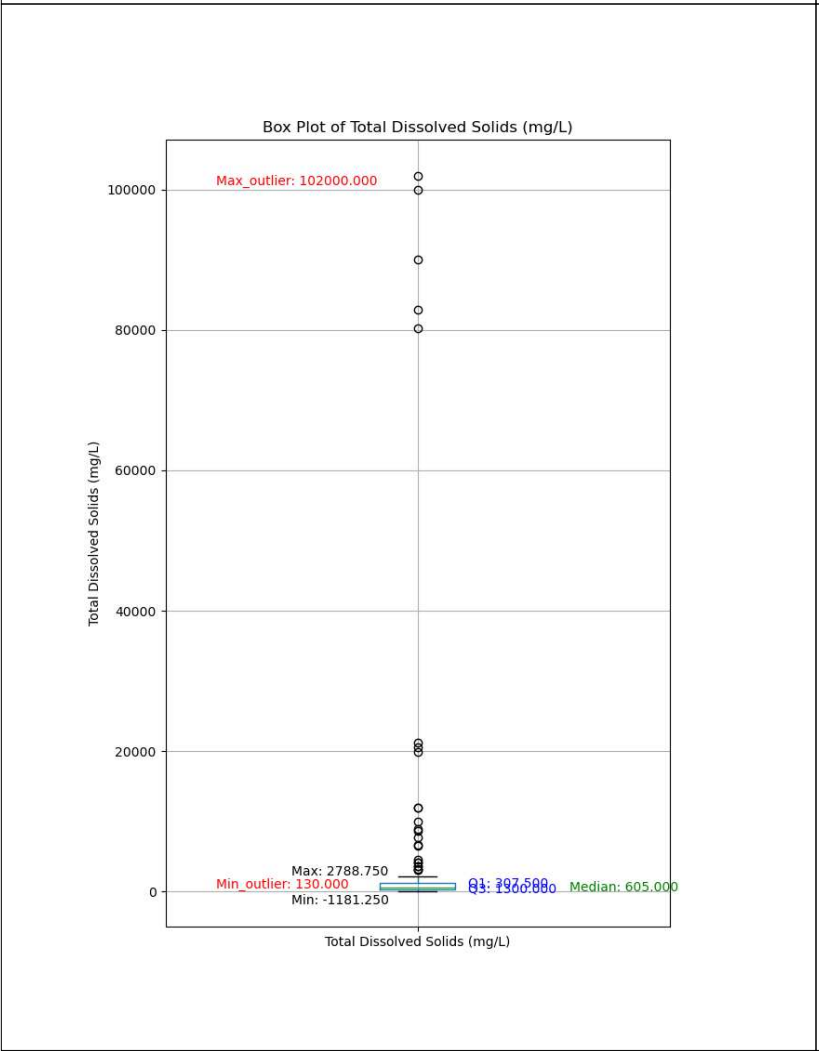

Box Plot of Sodium, Total Recoverable combined (mg/L)
Max_outlier: 8500.000
Min_outlier: 6.400
Max: 260.250
Min: -73.750
Median: 87.000
Sodium, Total Recoverable combined (mg/L)
Sodium, Total Recoverable combined (mg/L)

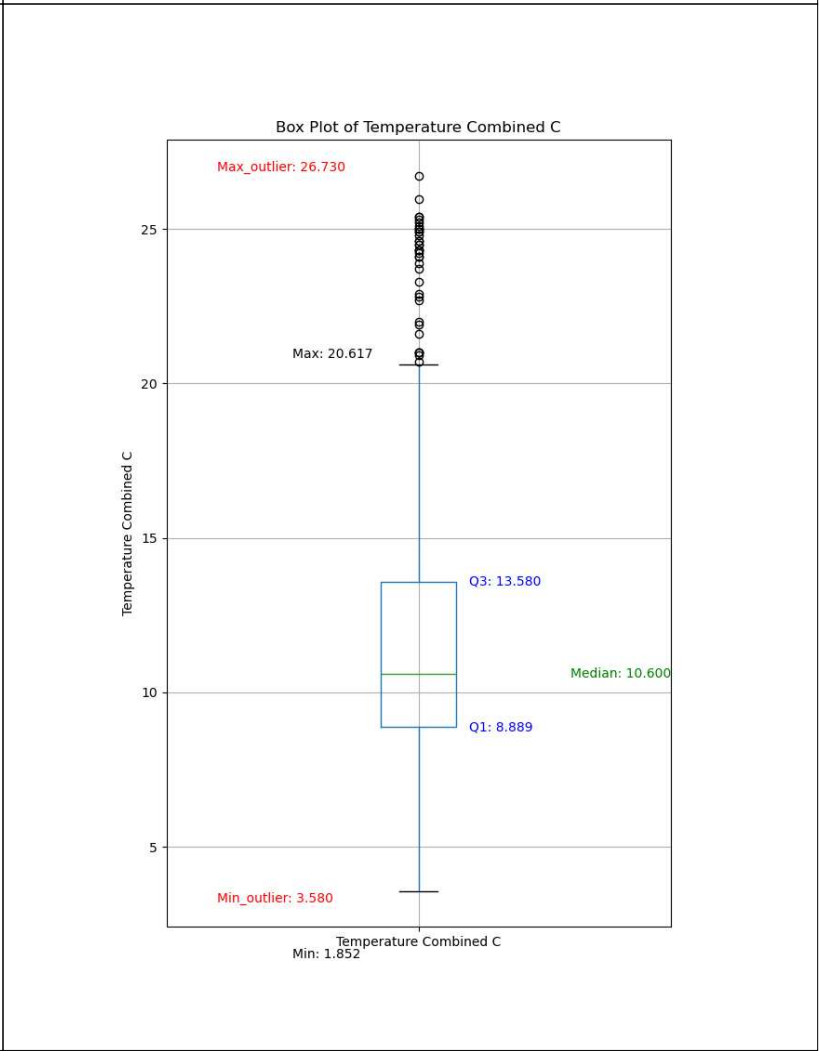

Box Plot of Strontium, Dissolved combined(mg/L)
Max_outlier: 940.000
Min_outlier: 0.010
Max: 3.479
Min: -1.844
Q1: 0.152
Q3: 1.482
Median: 0.575
Strontium, Dissolved combined(mg/L)
Strontium, Dissolved combined(mg/L)

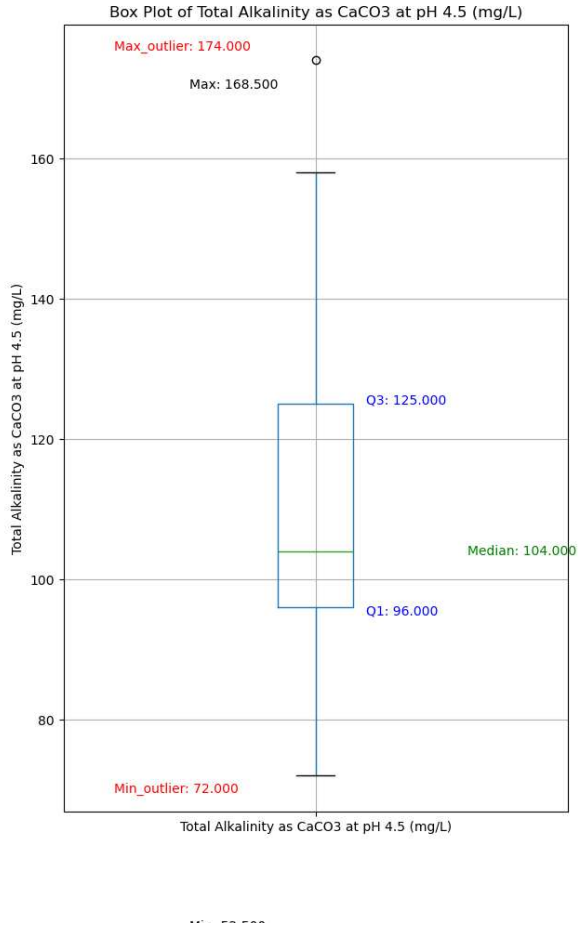

Box Plot of Strontium, Total Recoverable combined(mg/L)
Max_outlier: 410.000
Min_outlier: 0.000
Max: 4.814
Min: -2.296
Q1: 0.370
Q3: 2.147
Median: 0.920
Strontium, Total Recoverable combined(mg/L)
Strontium, Total Recoverable combined(mg/L)

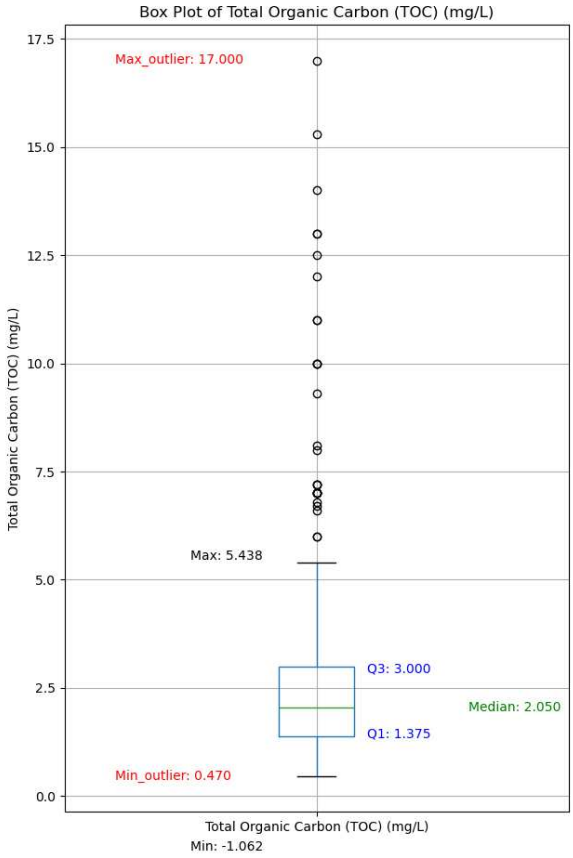

Box Plot of Sulfate (mg/L)
Max_outlier: 640.000
Max: 85.000
Q3: 40.000
Median: 28.150
Q1: 10.000
Min_outlier: 0.210
Min: -35.000
Sulfate (mg/L)
Sulfate (mg/L)

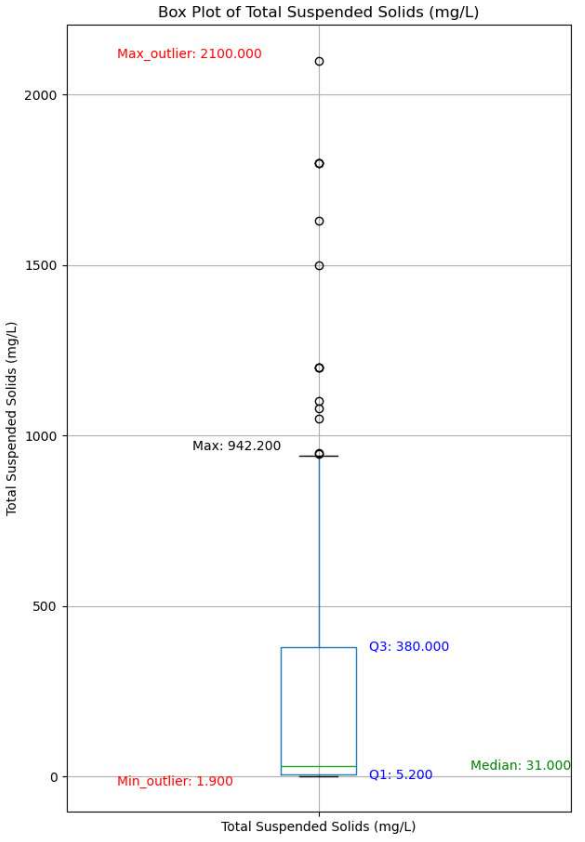

Box Plot of TDS (calculated) (mg/L)
Max_outlier: 244.000
Max: 188.000
Q3: 164.000
Median: 155.000
Q1: 148.000
Min_outlier: 129.000
Min: 124.000
TDS (calculated) (mg/L)
TDS (calculated) (mg/L)

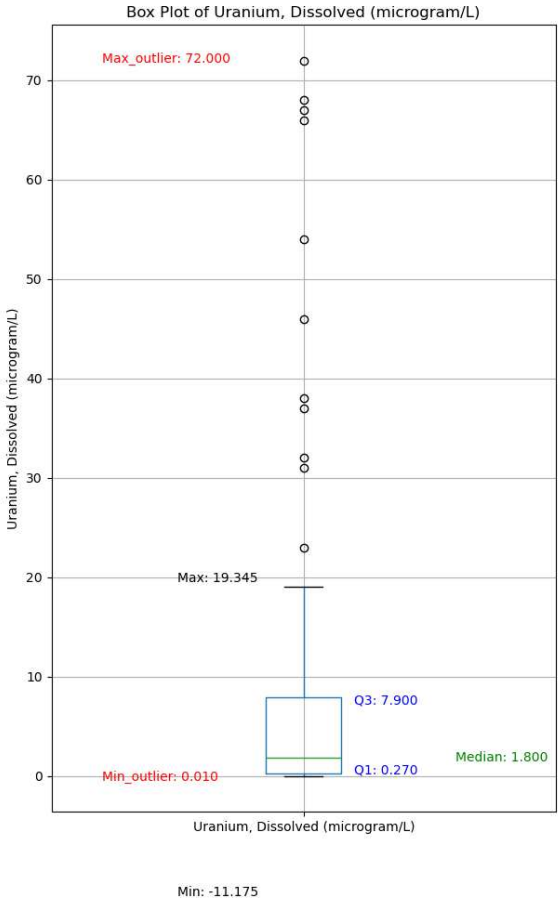

Box Plot of Total Dissolved Solids (mg/L)
Max_outlier: 102000.000
Max: 2788.750
Min_outlier: 130.000
Median: 605.000
Min: -1181.250
Total Dissolved Solids (mg/L)
Total Dissolved Solids (mg/L)

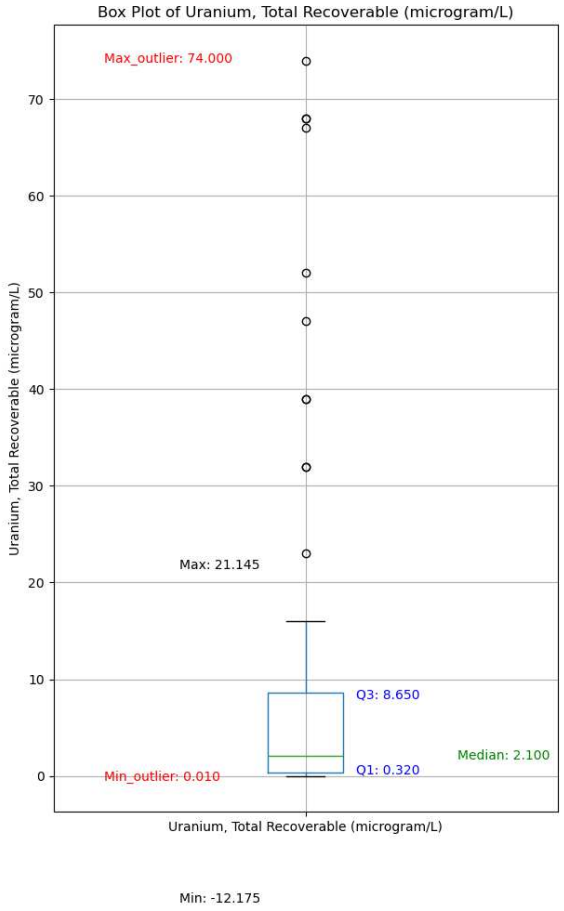

Box Plot of Temperature Combined C
Max_outlier: 26.730
Max: 20.617
Q3: 13.580
Median: 10.600
Q1: 8.889
Min_outlier: 3.580
Min: 1.852
Temperature Combined C
Temperature Combined C

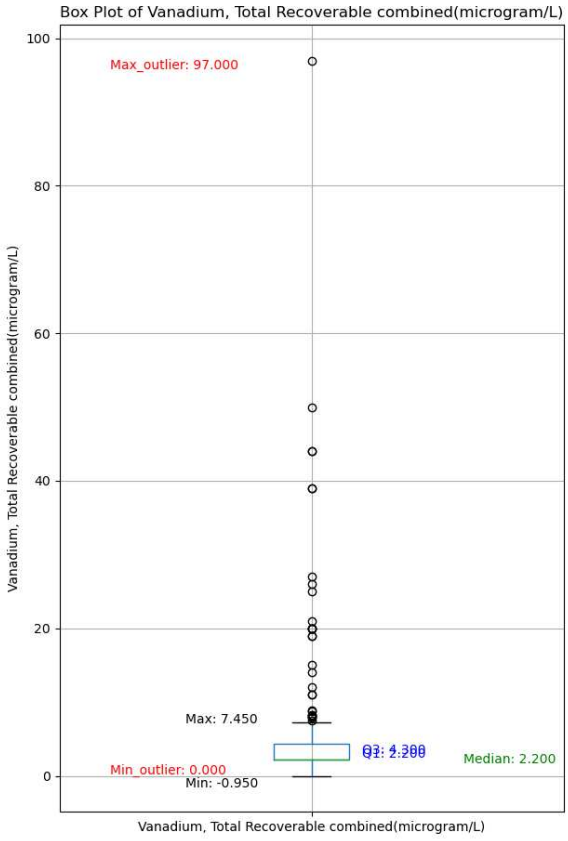

Box Plot of Total Alkalinity as CaCO3 at pH 4.5 (mg/L)
Max_outlier: 174.000
Max: 168.500
Q3: 125.000
Median: 104.000
Q1: 96.000
Min_outlier: 72.000
Total Alkalinity as CaCO3 at pH 4.5 (mg/L)
160
140
120
100
80

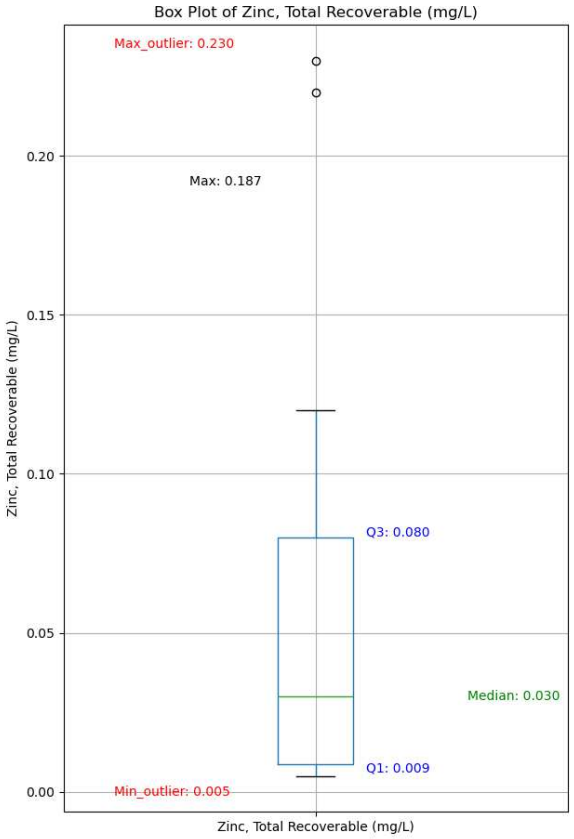

Box Plot of Total Organic Carbon (TOC) (mg/L)
Max_outlier: 17.000
Max: 5.438
Q3: 3.000
Median: 2.050
Q1: 1.375
Min_outlier: 0.470
Total Organic Carbon (TOC) (mg/L)
Min: -1.062
17.5
15.0
12.5
10.0
7.5
5.0
2.5
0.0


Box Plot of Total Suspended Solids (mg/L)
Max_outlier: 2100.000
Max: 942.200
Q3: 380.000
Median: 31.000
Q1: 5.200
Min_outlier: 1.900
Total Suspended Solids (mg/L)
2000
1500
1000
500
0


Box Plot of Uranium, Dissolved (microgram/L)
Max_outlier: 72.000
Max: 19.345
Q3: 7.900
Median: 1.800
Q1: 0.270
Min_outlier: 0.010
Uranium, Dissolved (microgram/L)
Min: -11.175
70
60
50
40
30
20
10
0


Box Plot of Uranium, Total Recoverable (microgram/L)
Max_outlier: 74.000
Max: 21.145
Q3: 8.650
Median: 2.100
Q1: 0.320
Min_outlier: 0.010
Min: -12.175
Uranium, Total Recoverable (microgram/L)
Uranium, Total Recoverable (microgram/L)


Box Plot of Vanadium, Total Recoverable combined(microgram/L)
Max_outlier: 97.000
Max: 7.450
Median: 2.200
Min_outlier: 0.000
Min: -0.950
Vanadium, Total Recoverable combined(microgram/L)
Vanadium, Total Recoverable combined(microgram/L)


Box Plot of Zinc, Total Recoverable (mg/L)
Max_outlier: 0.230
Max: 0.187
Q3: 0.080
Median: 0.030
Q1: 0.009
Min_outlier: 0.005
Zinc, Total Recoverable (mg/L)
Zinc, Total Recoverable (mg/L)